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Studies of Tars Produced by Low Temperature Carbonization of North Dakota Lignite

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STUDIES OF TARS PRODUCED BY LOW TEMPERATURE CARBONIZATION OF NORTH DAKOTA LIGNITE

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CERTIFICATE OF APPROVAL

This thesis, offered by Ber Lev, as a partial fulfillment of the requirements for the Degree of Master of Science in Chemical Engineering in the University of North Dakota, is approved by the Committee under whom the work has been done.

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Chairman

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II. Statement of Problem

The object of this research is twofold:

(1) The development of laboratory equipment suitable for the fractional distillation of lignite low temperature tar.

(2) Fractional distillation of an industrial low temperature lignite tar and a study of the fractions thus obtained.

III A.

REVIEW OF LITERATURE ON ISOLATION AND IDENTIFICATION OF LOW TEMPERATURE TAR COMPONENTS

A large number of chemical compounds can be recovered from the gas, liquor, and tar that are obtained as by-products in the destructive distillation of coal. Some of the substances thus recovered represent part of the volatile matter originally present in the raw coal. Other distillation by-products are formed by the thermal decomposition of volatiles and "fixed" (solid) carbonaceous matter, producing the so-called "primary" products. These primary products tend to crack and interact with each other as well as undergo many other chemical changes and produce, thereby, compounds that are known as secondary coal distillation products.

The physical characteristics as well as the chemical composition of the tar obtained in the destructive distillation of coal will vary with the following:

A. Kind of coal employed.

B. Temperature of carbonization.

C. Method of carbonization (e.g. vacuum, pressure, steam, etc.)

D. Rate at which hot gases are removed from the carbonizer and their rate of cooling.

E. Character of the scrubbing or recovery system.

In the case of low temperature tar, that is tar obtained on distilling coal up to 450-500°C., irrespective of the kind of coal, the general composition of the tar is similar in the sense that the same classes or types

of compounds are present. In a broad sense, the main difference is quantitative rather than qualitative. An analysis of the work done on low temperature tars can be used to advantage in formulating a method of approach to the investigation of North Dakota low temperature lignite tars.

The first important research on low temperature tars was carried out by Börnstein. (7) In 1904 he distilled eight Westphalian coals in 50° stages up to 450°C. On examination, the tar thus obtained was found to differ considerably both in physical characteristics as well as chemical composition from the more common high temperature tars. He found it rich in paraffins and higher phenols but could detect no naphthalene or anthracene.

In 1913, Pictet and Bouvier (33) distilled in vacuo, a bituminous coal from Montrabert at a temperature of 450°C. The tar yield amounted to 4 per cent by weight of the raw coal. The neutral protion of the tar was found to be made up chiefly of saturated and unsaturated hydrocarbons with traces of oxygenated compounds present. On fractionally distilling the neutral portion of the tar they succeeded in isolating hexahydromesitylene (C_9H_{18}), dihidrotrimethylbenzene (C_9H_{14}) as well as several saturated hydrocarbons.

Burgess and Wheeler (10) and Jones and Wheeler (21) prepared low temperature tars by vacuum distillation of English bituminous coals at 450°C. Burgess and Wheeler (10) subjected their tar to a preliminary fractional distillation at atmospheric pressure up to 300°C. They obtained a soft pitch residue which represented about 50-55 percent of the crude. This residue had a specific gravity at 15°C. of 1.128, and was entirely soluble in chloroform. The distillate was further fractionated and found to consist of the following:

(a) 40-45 percent of unsaturated hydrocarbons of undetermined composition, but richer in carbon than the olefines (C_nH_{2n}).

(b) 40 percent saturated hydrocarbons.

(c) 7 percent aromatic hydrocarbons.

(d) 12 percent of phenols, chiefly cresols and xylenols.

(e) a small amount of solid paraffins.

(f) traces of pyridine bases.

The American pioneers in the field of low temperature carbonization were Parr and Olin (31). Their objective was to obtain a good smokeless fuel from the low grade Illinois bituminous coals. In 1907 they conducted a series of experiments using superheated steam as an aid in removing volatiles from coal. As one of the by-products they obtained a dark brown tar of a specific gravity of 1.069. They refined this tar and then investigated its composition.

Their work was of considerable value, although in a number of respects it did not check very well with work done at a later date by other investigators. Thus, they reported the presence of considerable benzene, toluene, etc., which seems unusual in view of the fact that it has been proven by Whitaker and Crowell, (46) that these hydrocarbons first form at a temperature of 500°-600°C. for toluene, and 600° C. for the xylenes.

Fischer (16) appears to have been the first to take into account the thermal effects that may occur during the course of distillation, such as cracking and fixed gas formation. He noticed that above 300°C. these effects became sufficiently great to render any analytical work practically useless. He found that the greatest change takes place with the more viscous oils which are converted to low boiling and gaseous compounds. However, the only partially decomposed bitumen of the coal, the high boiling phenolic

compounds and the resinous matter, all of which appear in a low temperature coal tar are very reactive at temperatures near and above 300°C.

As a means for minimizing the thermal effects Fischer (16) suggested the use of extraction and chemical methods along with distillation, and the distillation at a very slow rate.

The decomposition of phenolic compounds at a temperature of 300°C. and upwards was investigated by Edwards (14). He found that water, homologues of phenol, aromatic hydrocarbons and a pitchy residue were obtained.

Weindel (46) continued this work by comparing tars which had been subjected to fractional distillation with those where no fractional distillation had been employed. His results checked with those of Edwards (14) and Fischer (16).

As has been mentioned, the cracking and decomposition of low temperature tar at an elevated temperature is further confirmed by the evolution of fixed gases. Thus Edwards (14) observed the evolution of SO_2 and H_2S at about 300°C., while Brittain, Howe, and Sinnatt (8), in their work with coalite tar, found that sulphur dioxide was evolved almost at the commencement of distillation while hydrogen sulphide first appeared at a temperature of about 170°C.

Weindel (46), in his work with low temperature tars, found that permanent gases began to be evolved at 275°C. with a maximum rate of evolution at 330°-340°C. The average amount of gas evolved during distillation to about 340°C. was found to be 16 liters per kgm. of crude. Its volumetric analysis indicated: 7 per cent H_2S, 4 per cent CO_2, 75 per cent methane and its homologues, 8 per cent ethylene and acetylene hydrocarbons, and small quantities of benzine-like hydrocarbons.

A distinct characteristic of low temperature tar distillate is the change of its color on standing. Shortly after formation it turns dark. A satisfactory explanation of this color change has as yet not been advanced.

Edwards (14) suggested condensation of phenolic bodies, with the formation of leuco-compounds such as rosolic acid and coumarone. Jaeger (20) assumed oxidation effects to be the primary cause in the darkening of distillate. He found that both light and the nitrogen bases in the distillate somehow promoted the darkening effect.

With a comparatively limited knowledge of distillation mechanics, and operating techniques, it was quite natural for many investigators to turn to the more difficult and painstaking, though at the time more accurate and reliable, methods involving extraction, solvation, derivative formation, etc.

In 1921, Kendall and Beaver (22) carried through an investigation of low temperature tar with the complete avoidance of fractional distillation. In brief, they first separated the oil into acids, nitrogen-bases and neutrals, following which they investigated each portion separately. They estimated the phenols by their freezing point effects and the nitrogen bases by their physical properties such as density, sp. gr. etc. With the hydrocarbons they employed a modification of the Tizard and Marshall aniline point method (40).

In this country, Morgan and Soule (28) investigated low temperature bituminous coal tar, similarly refraining from excessive use of distillation. In the case of the tar acid fraction they found that before the phenols and cresols could be identified, their homologues had to be

removed. Once that separation was accomplished the individual tar-acids could be identified quite easily in a number of ways. One method used by these investigators involved nitration to form nitro-derivatives. In another scheme they compared specific gravities of mixtures investigated with those obtained using synthetic mixtures. The hydrocarbons were separated into two groups, one containing paraffins and naphthenes and the other aromatic and unsaturated compounds by the use of 98 per cent H_2SO_4. The selective solvents, dimethylsulfate and selenium oxychloride, gave low results. The specific gravity and aniline-point method (40) was found inapplicable in the presence of unsaturated hydrocarbons. Physical methods, depending on refractive indices and specific gravities, were preferred in determining the proportion of naphthenes and paraffins to solubility in SO_2, miscibility with aniline and ultimate analysis.

At about the same time that Morgan and Soule (28) were investigating low temperature tars in this country, considerable attention was being directed to lignite tars in Germany.

Ruhemann and Rosenthall (38) made a thorough study of the neutral portions of gas producer tar from lignite. They first purified the crude by a method developed by Frank (17), extracted the neutral fraction and subjected it to fractional distillation, collecting the distillate at 5°C. intervals. Each of the fractions was then analyzed separately.

The lowest fraction b.p. 80°C. was clear, with a light yellow color. The next fraction had a blue fluorescence, while all of the higher fractions were opaque to light. All of the higher boiling fractions turned brown, even when kept in sealed glass containers, but regained their original appearance on redistillation.

In general, the neutral oils were found to be mixtures of pure hydrocarbons, sulfur, and oxygen compounds. Selective solvation was employed to separate the various compounds.

The work of Ruhemann and Rosenthall (36), was continued by Avenarius (3) and Vollmer (42).

Avenarius (3) concentrated on the tar acids with the view of investigating the phenols and carboxylic acids. He first steam distilled the crude tar to separate out the pitch. He then extracted the tar acids with NaOH, and fractionally distilled them (at 12 mm.) into 10°C. fractions. The fractions were each subjected to an elementary analysis indicating the following ethers:

(1) C_7H_{15} - COO - Me (b. 760mm. 206-216°C)

(2) $C_7H_{15}COO$ Me ($b_{15mm.}$ 143-153°C)

(3) $C_8H_{15}COO$ Me ($b_{15mm.}$ 173-184°C.).

The carbon contents were found to increase and the hydrogen contents to decrease with rise in boiling temperature. The acids of the lower fractions were found to correspond to the formula $C_nH_{2n-4}O_2$. They were then classified as to their cyclic character by interaction with bromine. It was found impossible to separate individual phenols by repeated fractionation at 12mm. pressure. The separation was accomplished, however, by transforming the highly fractionated phenols into esters of carbonic and allophanic acids by treatment with urea-chloride.

The esters were purified by fractional crystallization from benzene, petroleum ether and methyl-alcohol. Analyses of the carbonates and allophanates indicated that m-cresol, 1-4-5 xylenol, C_8H_9OH, $C_{IO}H_{13}OH$, unidentified thiophenols and unsatured phenols are all present in lignite creosote oil.

From a comparison of synthetically prepared esters with esters obtained from the creosote oil fractions it was further established that the phenols are constituted in part of m-cresol and 1-4-6 xylenol. The aromatic esters, unlike the corresponding aliphatic esters, could not be distilled at reduced pressures, because they are decomposed at temperatures close to their melting points.

Vollmer (42) made a study of the basic products above 160°C. He found these to consist chiefly of pyridine and quinoline derivatives which could be isolated by treatment of the tar oil with HCl and separation of the free bases by salting out with NaCl after liberation from their HCL solution by NaOH. The crude bases he then distilled, dissolved in dilute H_2SO_4, set free with KOH, steam distilled and extracted with Et_2O. He then evaporated off Et_2O and fractionally distilled the residual mixture. Compounds other than those already isolated by Sheder (38) were not found, that is only β and γ picoline, α and β lutidine and symmetrical collidine were isolated. With the fraction above 250°C. the method of Ahrens was employed and the bases were finally precipitated as picrates instead of the double mercury salts.

From the 250-5°C. fraction quinoline, isoquinoline, monomethyl quinoline, 3 isomeric dimethyl quinolines and a trimethyl quinoline, were recovered. In the 255-270°C. fraction, only quinoline was isolated. Above 270°C. crystalline picrates could not be obtained. From the distillation residue a monomethyl quinoline was isolated, which was probably a new isomer because the picrate (dark green scales m.p. 219°C.) corresponded to no known monomethyl quinoline or monomethyl isoquinoline.

Trutnovsky (41), in his researches in 1922 on the light hydrocarbon distillate from coal tar, developed a rather unique method of extraction by the use of activated carbon.

Referring to the methods described in the preceding paragraphs, it is obvious, that though quite accurate, their general utility, particularly where commercial development is considered, is very small. They are slow, elaborate, rather difficult, and too costly to be employed on a large scale. Hence, it is quite natural that many investigators in this field, encouraged by the remarkable progress made by petroleum industry in distillation technique, should turn once again to careful distillation as a general method for investigating low temperature tars. Thus, in 1926, Curtis and Beekhuis (13) made a study of low temperature Carbo-coal tar, first attempting, with but little success, straight distillation at atmospheric pressure. Their main difficulty was in the oxidation effects, which changed the nature of their tar. To eliminate these effects, they finally proceeded as follows: they distilled the tar into 15°C. cuts at atmospheric pressure, extracted tar acids from each fraction in the usual manner, formed the methyl ethers of phenolic groups, and subjected the methyl ethers thus obtained to very close fractionation at atmospheric pressure. In the case of each small fraction they determined its equivalent atomic weight by the Zeisel method in several series and checking their results by means of the Morgan and Meighan (24) method.

Caplan, Ross, Savage, and Swits (12) employed distillation methods only using an analytical still of the type developed by Peters and Baker (32). They limited their work to the 220-260°C. boiling range. The fraction boiling around 220°C. was shown to contain mesitol, that boiling at 234°C.

consisted mainly of 3 methyl 5 ethyl phenol. In general, the examination of the fraction of the acids up to 260°C. has indicated that they consist of mixtures of simple alkylated homologues of phenol.

In 1931, Herzenberg and Winterfeld (19) made a detailed study of lignite tar ketones. First the ketones of the lower boiling fractions were isolated as the phenolhydrazones, the crude ketones from which gave crystalline semicarbazones in good yields. Determination of the structure of the ketones proved difficult, however, as only in a few cases was enough material available. The 144-151°C. fraction gave an octanone (A) yielding valeric acid with CrO_3. Since the formation of ketones during the oxidation was not noted it is probable that (A) was a normal chain compound. The higher boiling fraction (167-170°C.) gave another octanone while the crude ketones of the fraction $b_{50\,mm.}$ 86-9°C. yielded at once large amounts of $CH_3.C_6H_5.C.NHNCONH_2$. From the higher boiling fractions of the tar oil the ketones were isolated as their $H_4F_e(CN)_6$ oxonium salts. The fraction $b_{12\,mm.}$ 54-120°C. gave several ketones of the composition $C_7H_{10}O$ and $C_8H_{12}O$ analyzed as semicarbazones.

Voznhinskaya, Pronina and Verentzov (43) investigated the neutral portion of low temperature tar, using distillation methods followed by chemical analysis. They found the oil to consist mainly of aliphatic hydrocarbons represented by both saturated and unsaturated groups, with aromatics present in insignificant amounts. Among the paraffin hydrocarbons were traced the series from C_7H_{16} to $C_{12}H_{26}$, the unsaturated hydrocarbons being represented by C_8H_{16} to $C_{12}H_{24}$.

In 1935, Morgan and Pettet (25) returned to the idea that distillation should be used sparingly in the analysis of low temperature tars because of the oxidation and thermal decomposition accompanying it. As an alternative they suggested a scheme in which at no time is it necessary to employ a temperature above 125°C. This method is really a modification of the one developed by Morgan, Pratt, and Ross (26). Phenols are first separated on the basis of their relative volatility with petroleum solvents and only then are they fractionally distilled at 0.01 m.m. Hg. The fractions are each identified by comparison with synthetic phenols (1) as well as sulfonation, (38) nitration, etc. outlined more fully as follows:

O-cresol (m.p.57°C) and m-cresol (b.p. 200-202°C) were isolated by sulfonation as suggested by Campbell (32); p-cresol (b.p.201°C. m.p. 30-34°C) was separated out by the method developed by Bentley and Cotlow (6); p-xylene was obtained by a scheme developed by Morgan and Pettet (27).

Aside from substances mentioned above, Morgan and Pettet (27) isolated the following compounds using selective solvents, forming derivatives and in general employing methods in which all reasonable possibility of decomposition was precluded: m-5-xylenol, o-4-xylene, 3-methyl-phenol, B-naphthol and α -naphthol.

In 1936 Stadnikov and Karakash (37) found that analytical methods used successfully in the petroleum industry are not directly applicable for investigating the aromatic and unsaturated components of low temperature tar because of the oxygen compounds present in the primary material.

Lander and McKay (23) in their book "Low Temperature Carbonization" classify low temperature tar components as follows:

A. Hydrocarbons

1. paraffins
2. ethylenes
3. cycloparaffins
4. acetylenes
5. benzenes

B. Compounds containing oxygen

1. alcohols (primary, secondary, and tertiary)
2. Phenols (various homologues and isomers)
3. aldehydes
4. ketones
5. acids

C. Compounds containing sulphur

1. hydrogen sulphide
2. carbon disulphide
3. mercaptans
4. thioethers

D. Compounds containing chloride

1. HCl
2. NH_4O

} Have been identified by Jones and Wheeler (35)

E. Compounds containing nitrogen

1. pyridine and its derivatives
2. picoline, its isomers and derivatives
3. collidine, its isomers and derivatives
4. quinoline and its derivative
5. toluidine, its isomers and derivatives

XII B

LITERATURE REVIEW

of

LABORATORY SCALE FRACTIONATION

Distillation theories and equations are fully discussed in the many books on that subject as well as general chemical engineering texts, such as Badger, McCabe (4), Walker Lewis and McAdams (44) etc. No attempt is made here to repeat the theoretical considerations involved.

Generally speaking, in the distillation of a multi-component system, advantage is taken of the fact that the more volatile constituents of a mixture of components, when partially vaporized, occur in increased concentration in the vapor phase. By repeated distillation or by distillation through a fractionating column, separation of the components of a vaporizable mixture can be effected.

In fractionation, use is made of columns or stillheads to complete the required separation in one operation. Obviously, fairly complete separation may be obtained with a binary mixture only.

In industry, fractionating columns may be (1) Sieve plate columns, (2) Bubble cap plate columns, (3) Packed columns.

When used in a continuous process the feed to the column is liquid, heated to near the boiling point or it may be part liquid and part vapor and enters at some point above the bottom plate. The lower plates act as stripping plates and remove the last traces of the more volatile component. Each plate acts in effect as a still, the composition of the liquid and vapour in its neighborhood remaining fairly constant so that a product of definite composition may be drawn off from any plate. Near the top of the

column concentration of the more volatile component is high. The heat necessary for vaporization, occuring on each plate, is provided by condensation of ascending vapours, while at the end other means are provided.

The separation of the constituents in an industrial column is dependent on the provision of reflux, that is, the return of part of the condensate down the column. In general, reflux at any point in the still will be richer in the more volatile component than the immediately ascending vapours; condensation of relatively greater amounts of the less volatile component will occur, followed by vaporisation of material richer in the more volatile component, the less volatile component being washed out of the vapour.

Fractionating columns may also be used in an intermittent manner. In this case the feed will be in the form of vapour from the mixture which is heated in a separate vessel, the still, and introduced at the lower column end. The composition of the liquid in the vessel, that of the vapour, entering the column and throughout the column will vary continuously with the progress of distillation. This is always the case in the usual laboratory fractionations using the usual stillheads, whether they be packed, bubble-cap type or have any other arrangement.

Distillation may be conducted at a pressure range from a fraction of a millimeter to hundreds of pounds per sq. in. depending on nature of material distilled, products desired and many other factors. Thus, vacuum distillation is employed primarily where boiling temperature lowering is required in order to reduce or eliminate thermal decomposition effects. Another advantage of vacuum distillation lies in fact that volatility differences of components are increased, so that closely boiling compounds may be separated. Volatility "v" is defined (44) as the ratio of the

equilibrium partial vapour pressure, "p", of a component in solution to its mol fraction, "c", in the liquid. Relative volatility is then the ratio of the volatility of one component to that of the other. Thus V=p/c. If the component obeys Raoult's Law in the mixture, p = Pc and it follows that v = P where P is the total vapor pressure. If the component obeys Henry's Law then p = kc and V at a given temperature is equal to the Henry's law constant K, at that temperature.

Vacuum distillation may be used directly in purification of compounds (51) or more commonly in separating components of a mixture reactive at elevated temperatures.

A survey of the literature on laboratory distillation equipment discloses many designs varying in size, construction material, type of packing, insulation, thermal and pressure control and other details depending on the character of the material distilled and the desired operating conditions. Thus, a study of the various available designs could serve only as a background for designing a tar distillation unit. A number of designs were selected, analyzed, combined, and modified to provide a starting point. During preliminary runs, various new features were incorporated, smaller difficulties ironed out and eventually a unit was developed which gave excellent results with the material on hand. The actual development work is discussed in a later section.

Reilly's text "Distillation" (35) was found very useful. Aside from a comprehensive discussion of theory it contains a very good review of laboratory fractionating units, including dimensioned sketches and numerous references.

Units developed by Podbielniak (34) were checked over, but were not thought suitable for the high boiling tar material on hand.

The first design considered was that of Peters and Baker (31). The essential features are a column packed with Raschig rings, a concentric hot-air jacket surrounding the column, a nichrome heating element spirally wound around column, to help maintain conditions within column adiabatic, a dephlegmator type reflux control and a receiver system which may be operated either at atmospheric pressure or at a vacuum.

The "true" boiling still of Beiswinger and Child (5) incorporates the electrically heated spiral evolved by Peters and Baker (32), though the hot air heater is substituted by a heavy layer of magnesia insulation. A receiver arrangement involving two receivers and a three-way stop cock makes it suitable for vacuum work.

Bush and Schwartz (9) in 1932 constructed an analytical still similar to the ones of Peters and Baker (32) and Beiswinger and Child (5) except for a rather efficient reflux control designed by the authors at an earlier date. In brief, it involves complete condensation of vapors followed by division of flow in an adjustable mercury trap. The advantages of that type of reflux-control are ease of regulation and independence of operating temperature and pressure.

In designing a still, particularly an analytical still, a number of factors must be considered aside from construction of shell, column condensers, and receiving system. Among the important factors are the selection of material, proper pressure and temperature control, etc.

Insofar as column packing is considered, a number of materials are available. With the exception of the comparatively recently developed helices (15), claimed to give improved separation, and the variety of Raschig

rings, none seem to be very popular for laboratory columns.

Pressure control equipment, though appearing in many forms, involves a vacuum pump operated intermittently or continuously, an electrically or magnetically operated monostatic relay and a valve connecting and cutting off system from pump.

Huntress and Hershberg (10) present a rather good survey of literature since 1940 on automatic pressure and vacuum regulating equipment. They also developed a very sensitive pressure control unit activated by a thermionic relay. Their original design was modified and improved upon by Falkin and Nelson (30) in 1934, while in 1935 Falkin (29) converted it into a movable, compact unit.

Temperature regulation is provided in all cases by rheostats, with thermometers, and in a few instances thermocouples are used to indicate temperatures.

IV.

MATERIAL USED

The primary tar used as the starting material in this research was obtained from the Lehigh Briquetting Company who operate a lignite briquetting plant at Lehigh, North Dakota. The plant is equipped with two Lurgi carbonizers, and the other necessary equipment for the production of briquettes and recovery of tar.

The carbonization is carried out at an average temperature of 500°C. (25°) and roughly atmospheric pressure.

The vapor scrubbing system includes a direct contact water-precooler where the temperature of gas is lowered to 90°C., a cottrel precipitator, a secondary cooler followed by a scrubbing tower provided with wooden grids to knock out any residual tar particles. A fan located between the cottrel and the secondary-cooler maintains a fairly fast rate of vapor movement.

The primary tar is stored in large steel tanks, provided with steam coils, in order to partially dehydrate tar. From here it is pumped to the batch distillation units.

The coal used as raw material is lignite obtained from a mine on the plant grounds. Two representative analyses of that coal are given in Table I, while that of stripped carbonizer gas is given in Table II.

TABLE I

Proximate Analysis of Lehigh Coal

(as received basis)

	I	II
Moisture	42.2	40.2
Volatile Matter	25.2	27.4
Fixed Carbon	23.8	27.5
Ash	8.8	5.0
Sulfur	0.26	0.25
Btu./lb.	6068	6519
Softening point of ash (°F.)	2250	2320

TABLE II

Orsat analysis of Stripped Carburizer Gas

Constituent	Percent by volume
CO_2	13.6%
Illuminants	0.4%
O_2	0%
CO	12.2%
H_2	23.8%
CH_4	11.6%
N_2	38.4%

The tar was received in 5-gallon tin cans. It had a syrupy consistency of dark color and had a pungent odor. On heating to about 90°F. it turned to a heavy oily liquid.

TABLE III. A.S.T.M. Distillation Results of Lehigh Crude.

(Designation D 402 - 36)

Sample Number I

Volume of Sample 99.50 cc.

Weight of Sample 103.10 gm.

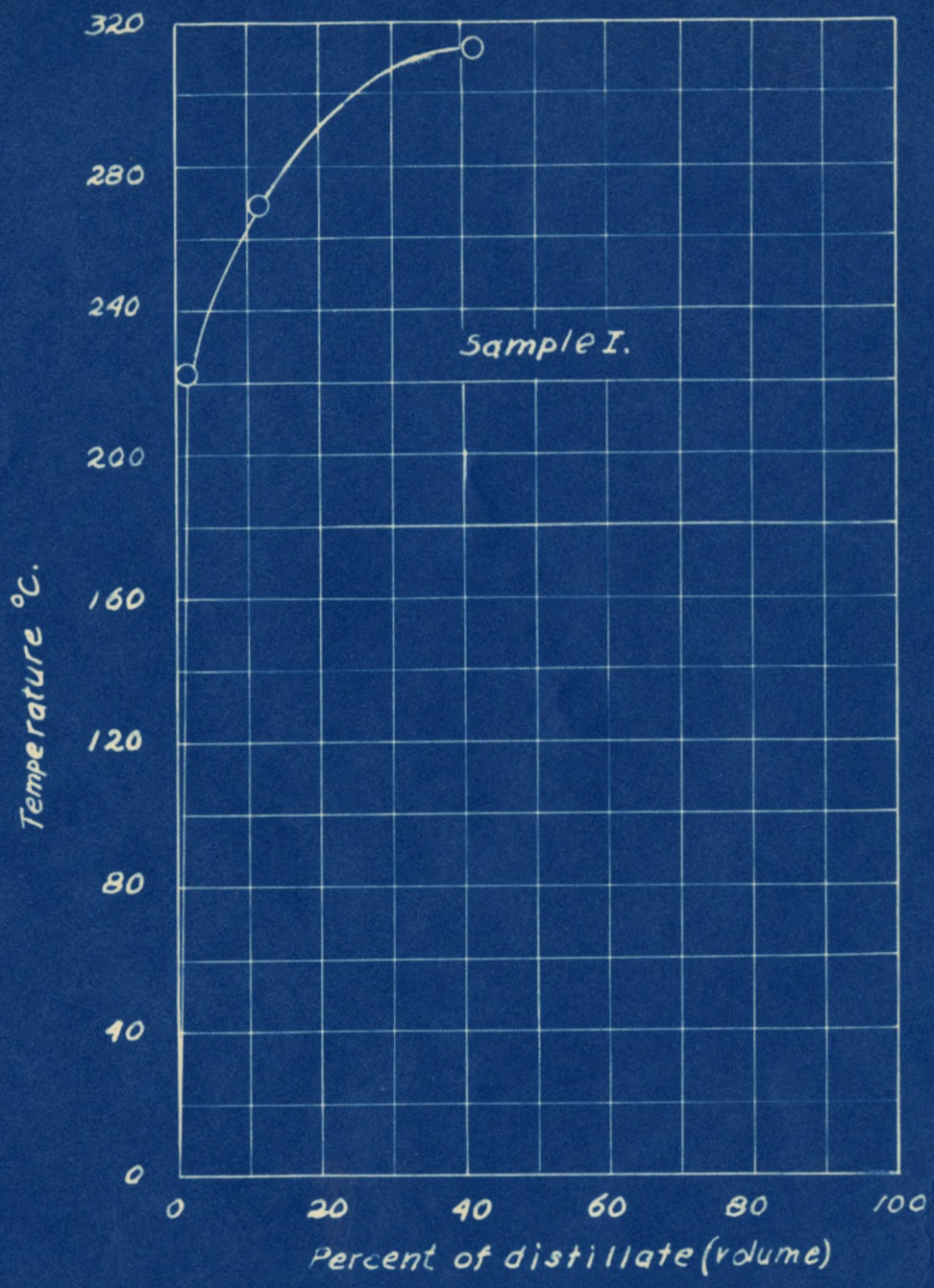
Temperature °C.)	Volume (cc.)	Percent by Volume (%)	Cumulative Percent by Volume (%)	Weight (gm.)	Cumulative Weight (gm.)	Percent by Weight (gm.)
Up to 225	0.65	0.65	0.65	0.46	0.46	0.44
225-270	11.60	11.45	12.10	11.73	12.18	11.40
270-315	29.90	30.00	42.10	30.90	45.08	29.91
Residue	56.80	57.10	99.20	56.00	101.98	57.20
Loss	0.85	0.80	100.00	1.12	103.10	1.05
Total	99.50	100.00		103.10		100.00

Sample Number II

Volume of Sample 98.50 cc.

Weight of Sample 102.00 gm.

Temperature °C.)	Volume (cc.)	Percent by Volume (%)	Cumulative Percent by Volume (%)	Weight (gm.)	Cumulative Weight (gm.)	Percent by Weight (gm.)
Up to 225	0.60	0.64	0.64	0.45	0.45	0.44
225-270	10.70	10.88	11.52	11.01	11.46	10.81
270-315	30.95	31.44	42.96	32.00	43.46	31.40
Residue	55.50	56.25	99.21	57.60	101.06	56.42
Loss	0.75	0.79	100.00	0.94	102.00	0.93
Total	98.50	100.00		102.00		100.00



Graph I. A.S.T.M. distillation curve for Lehigh crude tar.

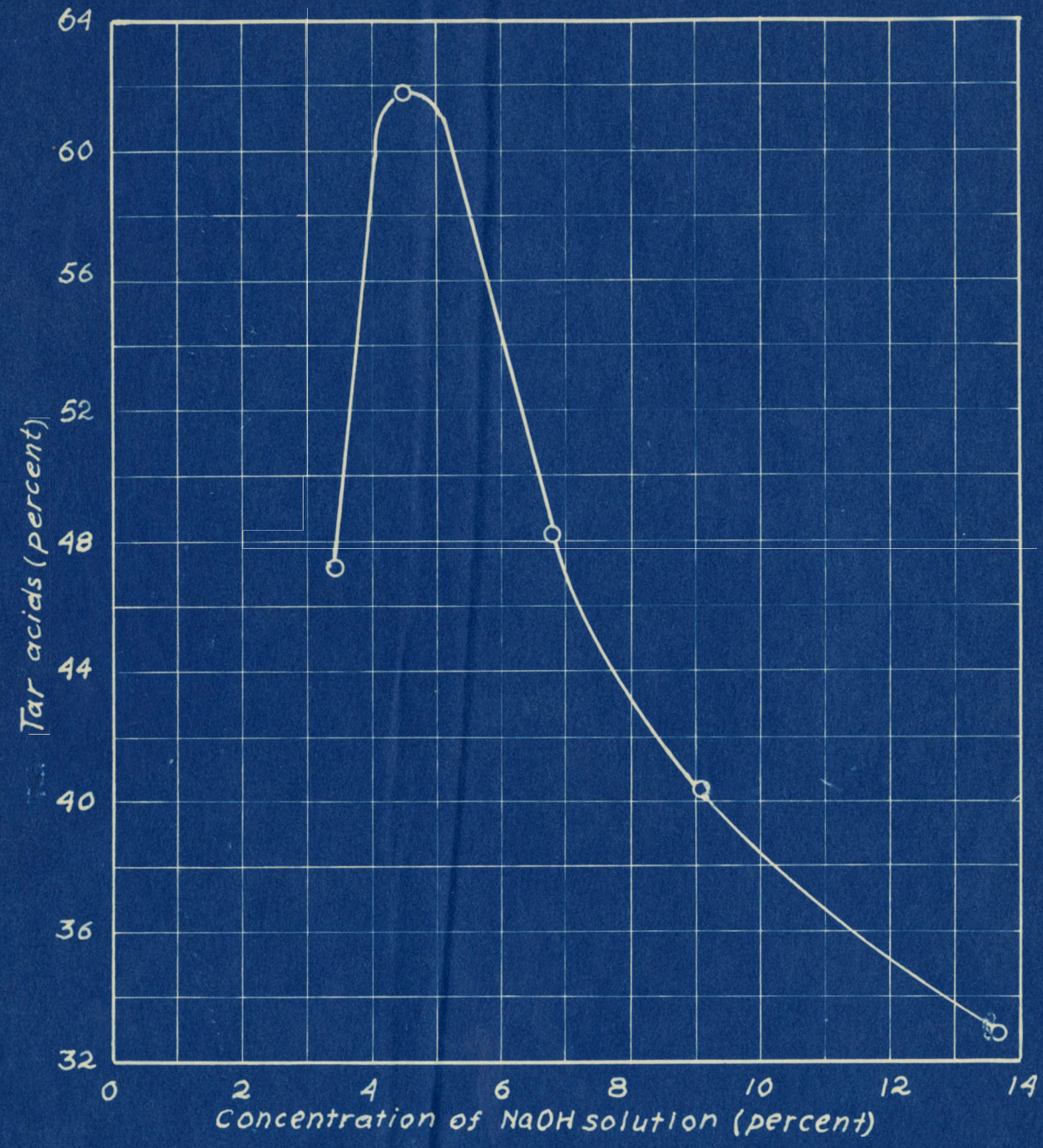
The specific gravity of tar as determined by the pycnometer method according to the A.S.T.M. designation D70-27, was found to be 1.0304 at 20°C. referred to water at 20°C.

A series of A.S.T.M. distillations (2) were carried out (Designation D402-36), though in neither case was it found possible to go much above 300°C. Fixed gas formation commencing at about 290° - 310°C. caused erratic temperature fluctuations, and rendered results obtained thereafter useless. This gas formation has been observed by other investigators. Apparently only heavier components of crude are thermally decomposed at 300° - 400°C. for later on, in distilling creosote oil obtained from the primary tar (Table VII) no noticeable fixed gas formation took place even at 330°C.

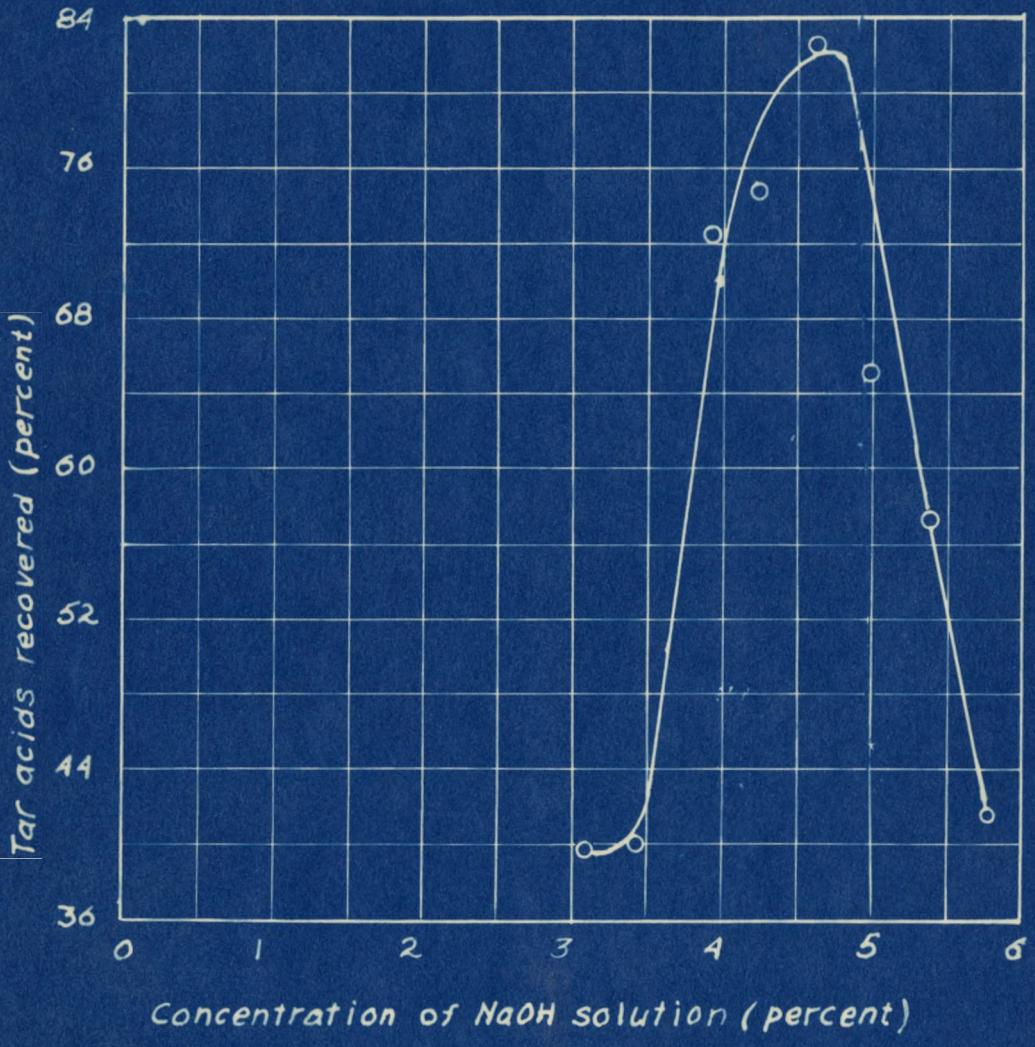
Typical distillation results carried to a temperature of 315°C. are given in Table XII and Graph 1.

A series of experiments were carried out, by the method of Morgan and Soule (24), with the crude to determine the optimum concentration of NaOH required to extract tar acids, as well as to determine the actual tar acid contents of crude. First, the approximate range was determined as summarized in Table IV and Graph 2. Following that, the exact range was determined as indicated in Table V and Graph 3.

As can be seen, the best results are obtained with dilute alkali solution. A 4.62 percent solution yields the highest value.



Graph 2. Approximate optimum concentration of NaOH required in the extraction of tar acids.



Graph 3. Optimum concentration of NaOH required in the extraction of tar acids.

TABLE: IV. Approximate Optimum Concentration of NaOH Required To Extract Tar Acids from Lehigh Crude Tar

Sample Number	Concentration of NaOH (%)	Weight of Sample (gm.)	Tar Acids Recovered (gm.)	Percent of Tar Acids recovered (%)
1.	3.44	41.95	19.70	47.10
2	4.55	52.95	32.50	61.80
3	6.89	44.35	21.40	48.10
4	9.10	63.01	25.65	40.80
5	13.80	64.00	21.40	33.10

TABLE V. Optimum Concentration of NaOH Required to Extract Tar Acids from Lehigh Crude Tar

Sample Number	Concentration of NaOH (%)	Weight of Sample (gm.)	Tar Acids Recovered (gm.)	Percent of Tar Acids Recovered (%)
1	3.06	39.90	1505	37.60
2	3.46	54.60	21.70	39.60
3	3.96	56.30	40.90	72.60
4	4.24	58.45	43.90	75.00
5	4.62	61.29	50.45	82.40
6	5.00	60.80	39.19	65.00
7	5.39	66.90	38.30	57.30
8	5.77	70.45	30.00	42.80

V A.

DESIGN OF EQUIPMENT

INTRODUCTION

Reference to the A.S.T.M. distillation curve (Graph 1) shows that the largest volume range (up to 300°C.) is included within about 100 degrees, (200° - 300°C.), comprising 35-45% of crude. It was decided, therefore, to concentrate this research on that fraction of the tar. Because ultimate separation of the constituents was to be made by distillation methods only, the final cuts had to be taken at very close intervals to isolate the desired compounds. Thus, with a 100° range, 0.4°C. intervals, 250 c.c. samples (assuming all final samples to be of equal volume), some 5000 c.c. of oil were required. In addition, quantities were needed for subsequent testing, making the required total about 8000 c.c. This involved the distillation of 15,000 - 20,000 c.c. of crude.

Such a large quantity of crude could not very well be handled in a small unit. On the other hand, the larger the still, the smaller is the accuracy because of entrainment losses, etc. Therefore, it was decided to construct two units: a large unit for handling crude, and for separating the oil into several close fractions; and a small still to reduce each of samples thus obtained to 0.4 - 0.5°C. cuts.

To reduce contamination, catalytic effects and interaction with any metallic surface to a minimum pyrex glass was selected as the construction material.

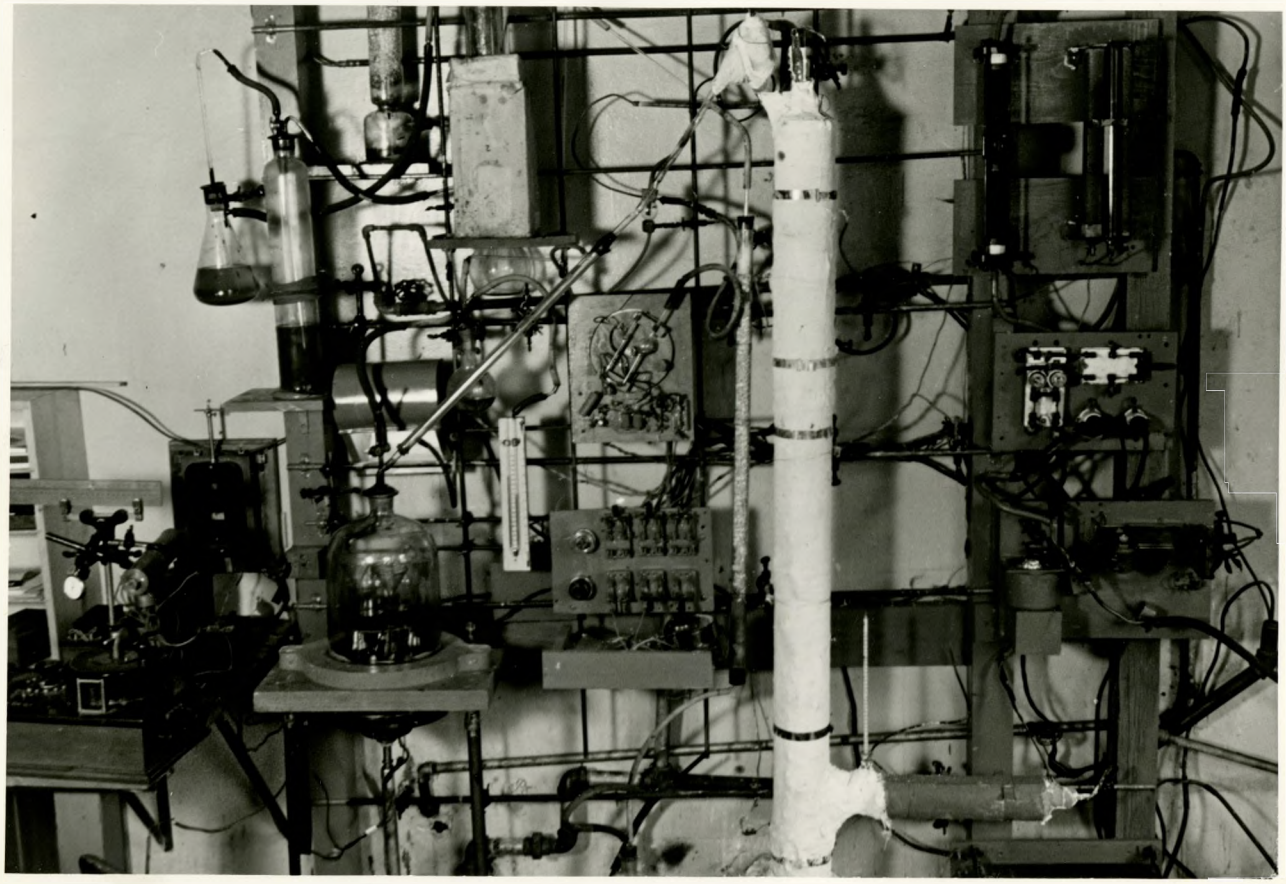


Figure 1. Crude-Tar Analytical Still.

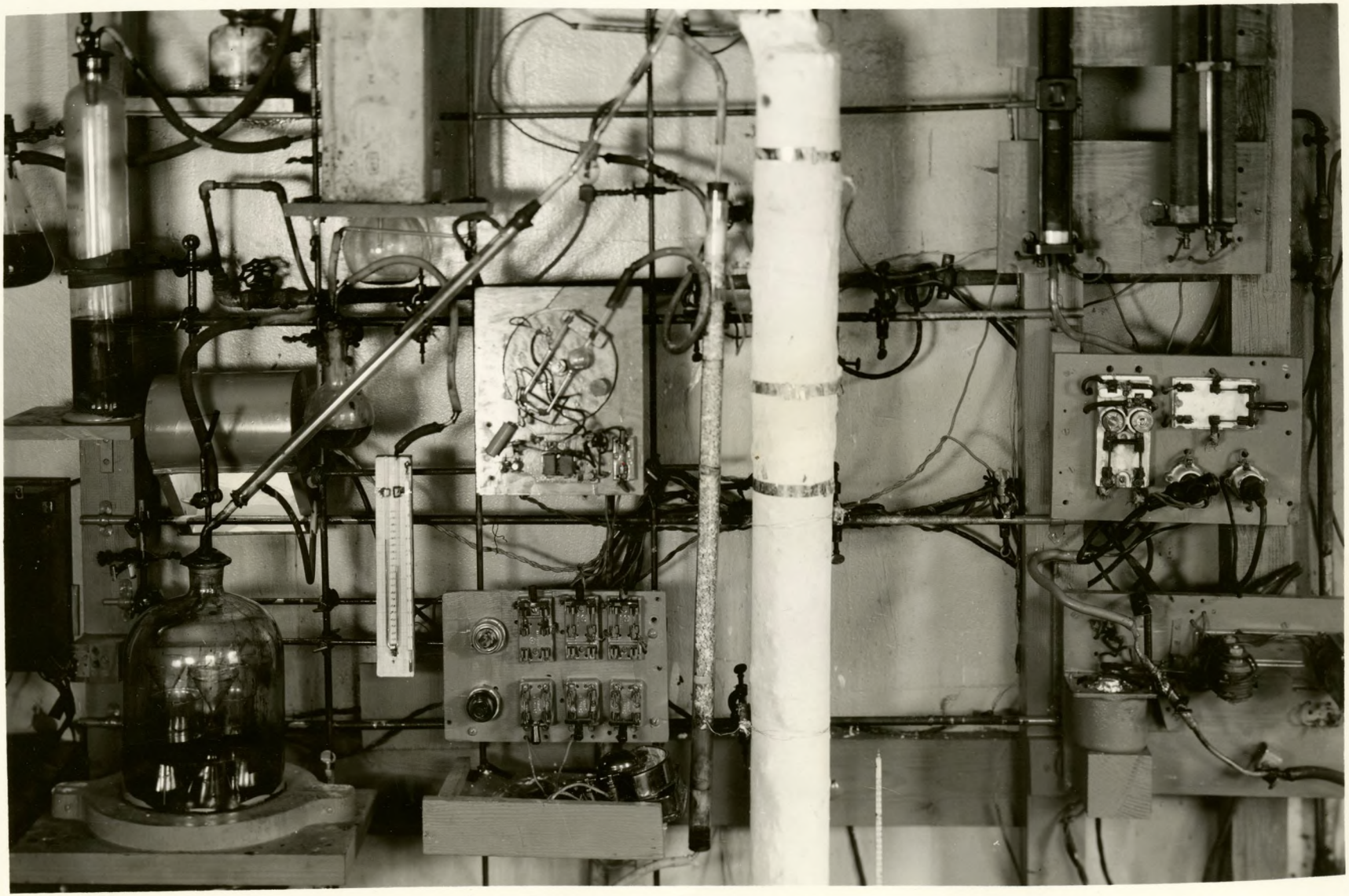


Figure 2. Partial View of Crude-Tar Analytical Still.

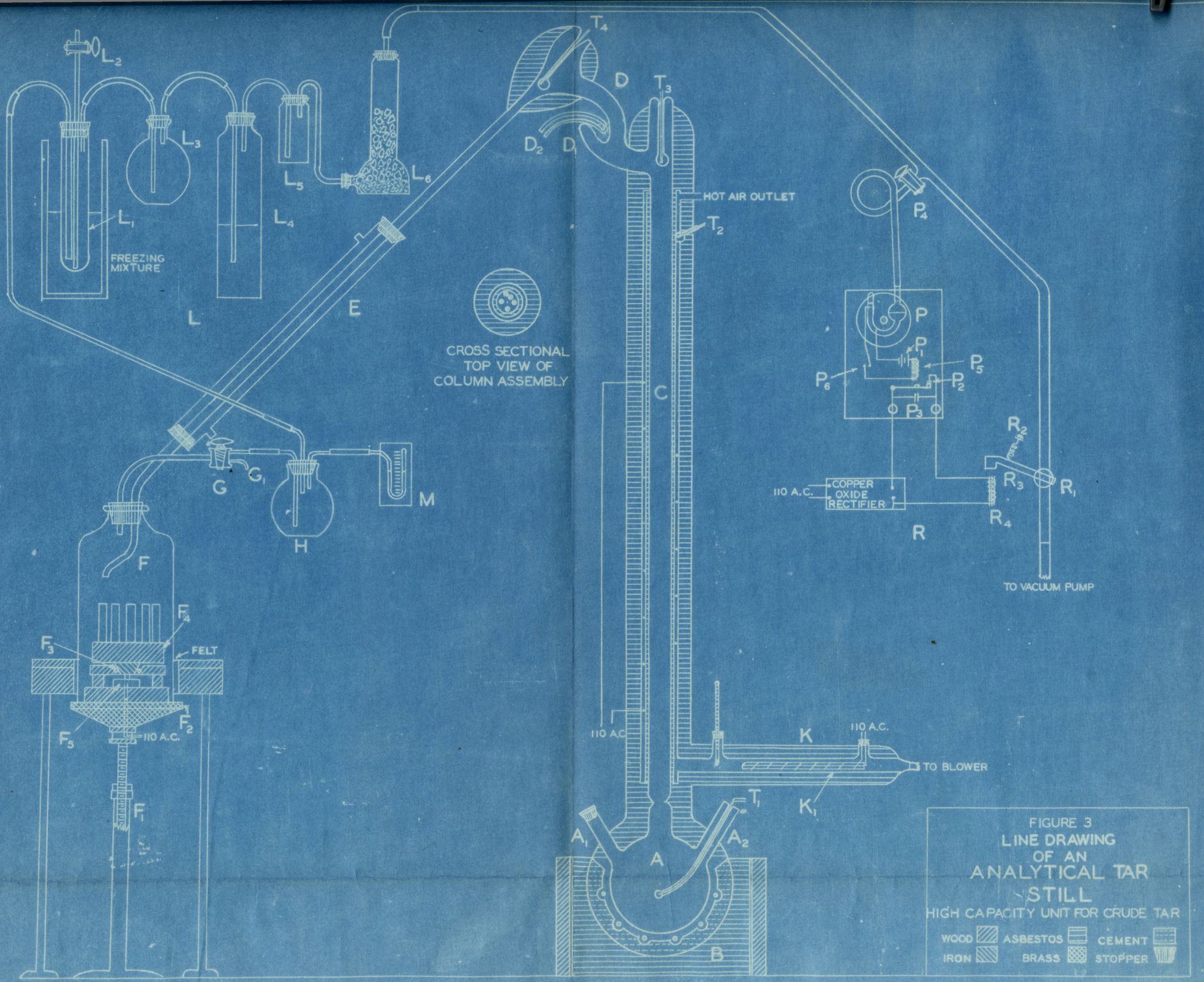


FIGURE 3

LINE DRAWING OF AN

ANALYTICAL TAR STILL

HIGH CAPACITY UNIT FOR CRUDE TAR

WOOD ASBESTOS CEMENT

IRON BRASS STOPPER

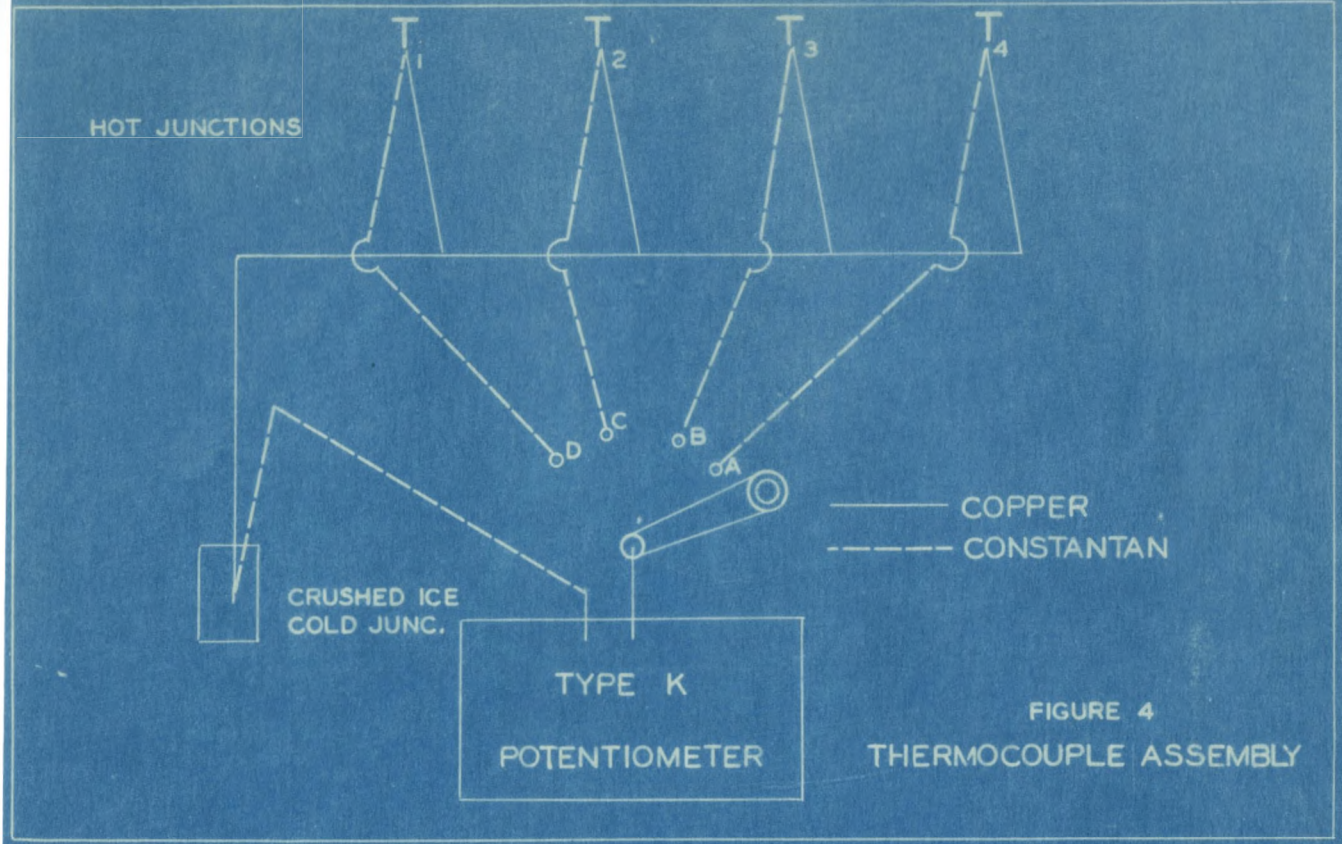
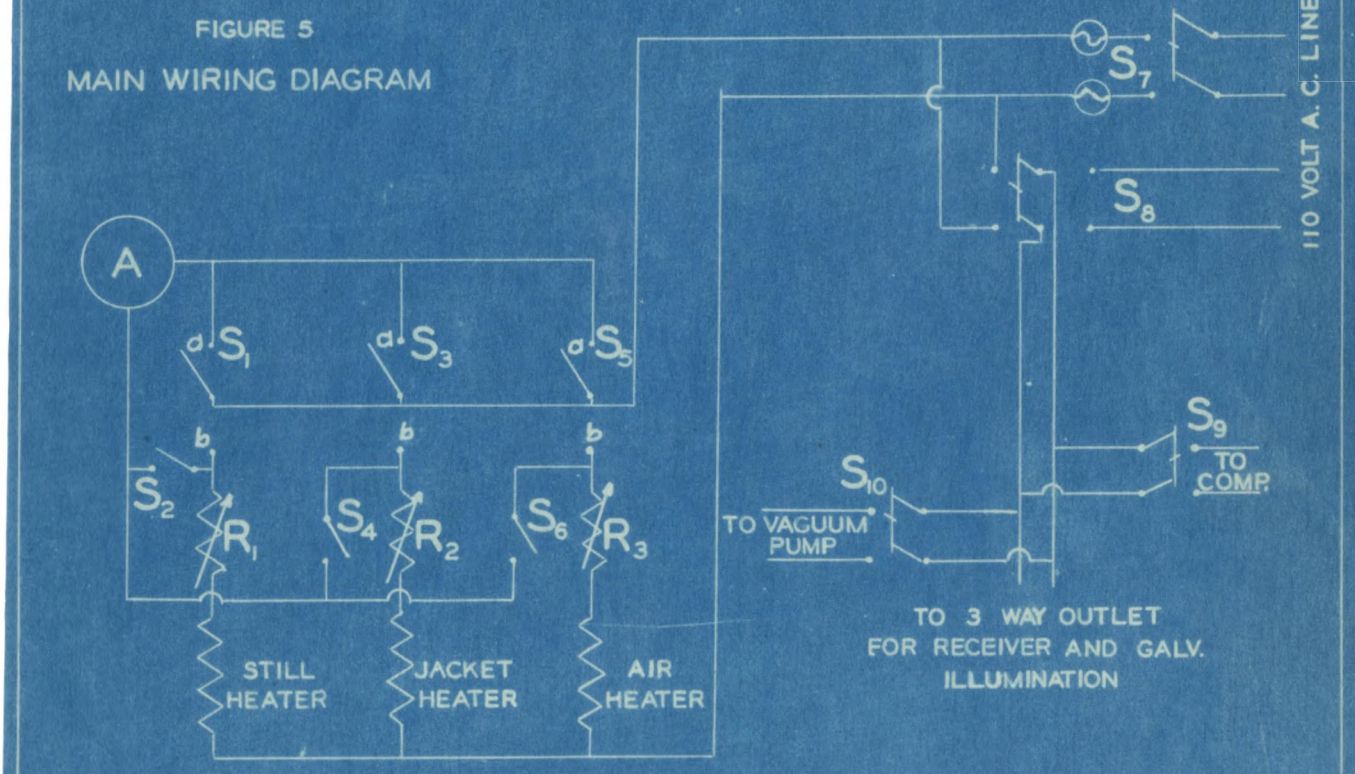


FIGURE 4
THERMOCOUPLE ASSEMBLY

FIGURE 5
MAIN WIRING DIAGRAM



V B

CRUDE TAR UNIT

Figures 1 and 2 are photographs of the larger unit; Figure 3 is a line drawing of the working assembly, while Figures 4 and 5 are wiring diagrams, shown separately for the sake of clarity.

In brief, the unit consists of still (A), fitting snugly into heater (B), and attached by a glass to glass seal to column (C). Reflux control (D) connects the column to condenser (E), whose inner tube extends into bell jar (F). A two way stopcock (G) serves to connect the still assembly to the absorption train and pump as well as to break the vacuum by admitting air through tube (K_1).

Still and Still Heater (Figure 3). The still consists of a 6 liter round bottom flask. The sidenock (A_1) 8 inches long and 1 inch in diameter, is used in filling it as well as in siphoning out the residue. When in operation, a rubber stopper wrapped with tinfoil is used to close off the tube. Since (A_1) is unlagged, the temperature about the stopper never reaches a point where foil would melt. (A_2) is a thermocouple well terminating in a little glass bulb filled with woods metal.

The flask fits into the specially constructed electrical heater (B). As indicated in diagram the heating coils are embedded in grooves formed in the high temperature (alundum) cement. Four No. 24 chromel wire heating coils connected in parallel and drawing a maximum of 12 amperes are used. The current is regulated, adjusted and measured by properly manipulating switches (S_1)(S_2), and rheostat (R_1) (Figure 5).

To decrease vibration strains, and to make the heating more indirect, a 1/8 inch layer of asbestos fibre is loosely packed between the still and the heater, and the cement heater shell is backed up by tightly packed asbestos, the whole unit being placed in a large tin can, rigidly attached to the floor.

The upper half of still is lagged with 2 inches of 85 % magnesia, provision being made for one peep-hole 1 inch in diameter.

Column and auxiliary equipment. The column assembly (C) consists of heating coil surrounding it, magnesia pipe covering, air heater (H), and small air blower (not indicated in either figure).

The column consists of a 5.5 foot glass tube, 1.576 inches O.D. At a distance of 2 inches from the still the column is indented inwardly about its circumference, forming a support for a conically shaped tube filled with small perforations. The column is then filled for a distance of 4.5 feet with ceramic Raschig rings 7/16 inches long and 7/16 inches I.D. The only other type of packing tried was that of 0.0787 - 0.1181 inch I.D. glass tubing cut into 1/4 inch lengths. However, that particular arrangement was found unsatisfactory because of high entrainment and excessive pressure and temperature differentials. In a number of runs where glass tubing was used as the packing, temperature differences of as much as 100°C. across the column were encountered. With Raschig rings, the temperature drop was reduced to 30-40°C. across the column, while entrainment was cut down to a negligible value.

Tightly wrapped around column and entirely covering it are strips of asbestos paper held in place at 7-9 inch intervals by chromel wire bands each terminating in a small hook. Loosely attached to these hooks is a 20

foot spiral of No. 18 chromel wire, connected through switches(S_3), (S_4), and rheostat (R_2) to the 110 A.C. supply. (Figure 8)

Surrounding the column, and forming an air jacket, is 6 inches O.D. magnesia pipe covering, 1 inch thick. It is cemented together at the joints by an 80-20 mixture of magnesia and plaster of Paris respectively.

A glass jacket was tried with the original design, but was found unsatisfactory because of heat losses to the outside, as well as fragility.

To prevent localization of heating effects and to help maintain conditions within the system adiabatic, preheated air is blown through the air space between the column and the jacket at a constant rate. A small Cenco centrifugal blower belt driven at 2500 r.p.m. by a 1/4 h.p. motor supplies the air stream.

The air heater (K) is similar in its construction to the one designed by Peters and Baker (31). It is constructed of a glass tube (K_1) 20 inches long and 1.57 inches O.D. One end fits into the column jacket, while the other end is tapered down to receive rubber tubing. The heater tube (K) has two side tubes sealed to it, one for a thermometer and the other for lead wired. Inside the tube, supported on porcelain strips, is a 11.5 inches long 0.7874 inches O.D. quartz tube about which there is wound a No. 24 chromel wire coil with a current carrying capacity of 5 amperes controlled by switches (S_5), (S_6), and rheostat (R_3). The wire is held on to the quartz tube by Insolute cement applied at a number of spots along its length. The glass tube is insulated by 1 inch pipe covering.

Reflux regulation. Reflux control (D) is connected to the column by a one inch tube sloping upwards to facilitate return of liquid. It is simply

a pear shaped piece of tubing 3 inches long and 1.5 inches O.D. at its widest point. Through a side opening in the column, a small well (D_1) is inserted and attached by means of an inner seal. Water is circulated through a removable "U" tube (D_2) placed in well. The condensed vapors trickle down the well, thereby enabling the operator to check on the reflux rate. It may be varied by controlling the amount of water circulated through the "U" tube, as well as by regulating the vapor-flow rate.

The uncondensed vapors rise through the reflux control past the couple well, and are drawn into the condenser line.

The reflux bulb is lagged with a 1 inch layer of magnesia except for a section about the lower part of the well which is left uncovered for observation.

The reflux control just described was found easy to operate and adjust, and was developed after several unsuccessful attempts with other types of reflux regulating equipment. Thus, more specifically, the Peters and Baker (31) type involving a reflux condenser placed vertically above the column, was found to promote excessive condensation of tar vapors, and was generally quite difficult to manipulate. The Bush and Schwartz (9) reflux regulator involving complete condensation and division of flow by an adjustable mercury trap was used for some time and with a fair degree of success. It was later modified. The plunger was replaced by an ordinary rubber bulb, filled with mercury, and a stopcock was inserted between the trap and the bulb. To adjust the reflux it was simply necessary to open the stopcock, allow mercury to flow back or force more of it into the trap and close the stopcock again. Obviously, this kind of regulation could be employed both under vacuum as well as atmospheric pressure. However, because of entrainment of distillate in the trap, and hence contamination of successive fractions,

it was finally replaced by the device already described.

Condenser (E). A continuous 0.433 inches O.D. tube leads from the reflux control to the receiver system. A 0.5906 inches I.D. tube 2 feet long, placed concentrically with distillate tube serves as condenser jacket. It is held in place by means of rubber stoppers, and is provided with water inlet and outlet forming a simple Liebig condenser.

Receiver System. The receiver assembly is located within a bell jar (F) (10 x 18 inches) held securely in a wooden frame that is lined with felt-cloth. The bottom of the jar is closed off by means of a smooth circular brass plate (F_2), which is raised or lowered with screw jack (F_1). Beeswax helps to maintain a vacuum tight joint between the plate and jar.

Resting on the plate is a circular wooden base 1 inch thick and 9.75 inches in diameter. Secured to that base by means of 2 screws is an electric clock mechanism including a motor and part of a gear system (F_5). A small shaft 1/8 inch in diameter is soldered vertically to the shaft of the gear which rotates at about 10-15 r.p.m. It is this shaft which provides motive power for turntable (F_4).

Nailed to the edges of the base are two small wood blocks 1.5 inches supporting a board 2 x 9 x 1 inch thick. A small automobile roller bearing (F_4) is firmly wedged into a hole that is drilled in the center of the board. A piece of wood 2 inches in diameter is firmly wedged into the bearing forming a shaft. The lower end of that bearing-shaft has a small 1/8 inch hole drilled in it through bottom to receive the motor shaft. An ordinary wood screw put in through the side holds the bearing shaft and motor shaft firmly and prevents any slipping effect. The upper end of the bearing shaft supports a circular turntable 8.5 inches in diameter attached to the shaft by means of three small wood screws.

About the circumference of the turntable, holes are drilled at regularly spaced intervals, reaching only part way through the wood, and serving as test tube holders or flask holders. Thus, by using different turntables, almost any kind, shape, or size of receiver, can be used.

The motor lead wires pass through a small hole drilled in the center of the brass plate and filled with De-Khotinsky cement to a key switch located near potentiometer (Figure 1), and on to the 110) A.C. supply. For operation it is only necessary to tap key-switch and thereby move the turntable until the desired receiver is directly under the distillate outlet. Enough receivers are placed on the table for an entire run and they are filled consecutively without any possibility of contamination or air leakage.

Other methods of collecting condensate were tried but found to be unsuccessful. Thus, the Beiswinger and Child (5) vacuum receiver system, involving a three-way stopcock and two receivers, so as to enable the operator to empty one receiver while the other is filling caused difficulty with leakage through the stopcock, impossibility of cleaning receivers in short time limit between fractions, and danger of breakage because of necessity to manipulate stopcocks rapidly. Specially compounded high vacuum greases seemed to help for short periods of time only.

The ordinary dessicator type receivers caused trouble because of difficulty in twisting stoppers, or ground glass joints under high vacuum, without promoting leakage, and causing strains in glass line.

Absorption System (L). A glass tube connects the receiver assembly through stopcock (G) to absorbtion system (L). Stopcock (G) is also used to break the vacuum by simply turning it so as to admit air through tube (G$_1$).

Flask (H) serves as a trap for any liquid carried over from the receiver or siphoned back from the absorption towers. It also serves as a connection to the manometer, which was inserted at that particular point rather

than following the absorption system, because of pressure drop across the towers, and also because of greater sensitivity obtained with this particular arrangement.

Next in line comes a thermos bottle filled with crushed ice and freezing mixture. Tube (L_1) serves as an additional trap for any highly volatile components. A central tube (L_2) provided with a stopcock is used in siphoning out accumulated condensate.

A 500cc. flask (L_3) follows the Dewar flask and is connected to a 2000 cc. cylinder (L_4) used as a sodium hydroxide tower. (L_5) is another 400 cc. bottle followed by a usual laboratory calcium chloride tower (L_6).

This rather elaborate absorption train was found necessary to eliminate completely the tar fume odor from the room and to prevent difficulties with back-siphoning of sodium hydroxide. From the calcium chloride tower a line leads to the vacuum pump. Ordinary copper tubing is used. A branch line brazed on to it is connected by means of vacuum tubing past a two-way stopcock to the manostatic relay. The manostatic control, involving a magnetically operated valve, is located in the main vacuum line, at a point past the relay.

Pump. A small Eisler pump directly geared to 1/6 h.p. motor is quite satisfactory both from the standpoint of durability as well as capacity. A Cenco Hy-Vac was tried first but was found too slow in evacuating the large system. A small flask attached with a clamp to the pump and directly preceding it serves as a trap for any liquid, dust or mercury carried over from the system.

Pressure Control. The success of an analytical still depends to a great extent on the constancy of pressure maintained within the system, hence the importance of a sensitive manostatic relay and control equipment.

In this particular instance the requirements weresa sturdy high capacity device entirely automatic in its operation, and one that could be constructed with a minimum of expense. The final form of the relay and the magnetic control are shown in their operating positions in photographs 1 and 2, while in Figure 3, with the aid of a somewhat simplified arrangement, the wiring involved is clearly indicated.

The relay(P) consists of: (1) A vacuum mercury manometer with arms 0.157 inches I.D. 12.6 inches high and 1.97 inches apart.

(2) An electric dry cell buzzer (P_2) and (P_5) in which hammer and gong are replaced by two iridium contacts, (P_2).

The manometer is mounted on a circular disc pivoted to the relay panel by means of a 3/8 inch stove bolt, (with burr towards outside). Several washers placed between the panel board and disc facilitate the turning of latter. Once the desired position is reached the bolt is slightly tightened by hand to prevent slipping of the disc. To adjust, the bolt is loosened and the disc turned until proper adjustment is reached. The manometer arm, connected by the stopcock (P_4) to the vacuum system is blown out in its middle section to form a bulb 1.181 inches in diameter. Thus, a slight fluctuation of mercury in the bulb (mercury half fills bulb) causes a proportionally greater degree of movement in the closed-end arm.

Two dumet wire contacts are sealed into the manometer as indicated in Figure 3 and are connected in series with two dry cells (P_1) and buzzer (P_5) and (P_2).

The actual pressure control involves an automatic magnetically operated valve (R_1) which cuts off or connects the system to the pump as may be required to maintain desired pressure. A gas pet-cock valve (R_1) serves the purpose. Both of its ends have brass tubing soldered on and held rigidly in position by means of clamps as indicated in Figures 1 and 2.

The valve plug handle has several 1/8 inch holes drilled in it and a 1/2 x 4 inches strip of iron serving as a lever (R_3) attached to it with small bolts. A soft iron disc 1/8 inch thick and 1.5 inches in diameter is brazed on to the end of the lever (Figures 1 and 2). Underneath that disc is placed a 110 D.C. electro magnet (R_4) so that disc super-imposes the magnetic core when the lever is lowered. To prevent the disc from sticking to the magnet its lower surface is tinned, though a piece of tinfoil or aluminum foil wrapped about the top of the core serves the purpose just as well. The lever is held and brought back to its rest position by spring (R_2) and end of which is inserted in a hole drilled in the lever, and the other attached to an iron strip projecting from the board over the lever (Figure 2). To adjust tension in the spring it is simply necessary to bend slightly the comparatively elastic strip supporting the spring, until the desired tension is reached. Since no very close adjustment is necessary this scheme is quite satisfactory. To facilitate its motion and minimize air leakage, the valve is lubricated with a mixture consisting of equal parts of stopcock grease, vaseline, and heavy lubricating grease.

In actual operating as relay switch (P_6) is closed, buzzer-electromagnets (P_5) draw the bell-hammer arm towards them thereby bringing the iridium contacts together. That in turn completes the circuit in the pressure control arrangement and activates magnet (Ra) which attracts the valve attachment and opens valve(R_1).

As the vacuum increases, the mercury level in the closed arm of the relay manostat falls until it just passes the dumet contact. That of course stops the flow of the current in the relay circuit; then the buzzer magnets release arm, which breaks the circuit in control (R_1) and enables the spring (R_2) to pull back lever (R_3) and thus cut off the system from pump. By turning manostat disc, the level of the mercury in manostat manometer is varied and hence the instrument can be adjusted to maintain any pressure up to 2 inches Hg. For higher pressures, the manostat can not be used since mercury in the evacuated end does not come down past electrical contact even when the instrument is tilted so that the arms are practically horizontal.

The main difficulty encountered with that arrangement was sparking across the iridium contacts. However, that was entirely eliminated by connecting a 50 microfarad condenser (R_3) across the contacts.

The actual pressure is noted by means of a small vacuum "U" manometer 0.118 inches I.D., 7. 1 inches long, with the arms 0.787 inches apart. A strip of graph paper graduated in millimeters and pasted in between the arms serves as a scale. Using a magnifying glass, the pressure may be estimated to one tenth of a mm. Only one reading is necessary per run since manostatic control maintains the pressure sufficiently constant. No fluctuations can be observed with naked eye in manometer (M.)

Temperature Measurement. Four copper-constantan couples (T_1), (T_2), (T_3), and (T_4) and one thermometer which is placed at the exit end of air heater (H) enable operator to determine temperatures at strategic points in the system. (T_1) measures the temperature of boiling liquid within still, (T_2) the temperature of the vapors entering the reflux control, and (T_4) temperature of the vapor entering condensing system. The e.m.f. generated by the couples is measured with a type "K" potentiometer used along with a sensitive D'Arsonval

wall galvanometer. (Figures 1, 2, and 4). A thermos bottle further insulated with magnesia, and filled with crushed ice provides an excellent cold junction. All junctions are formed by welding wires together with gas-oxygen flame using borax as flux.

Couples are protected from corrosion by being placed in thermocouple wells (Figure 3) each partially filled with Woods metal to improve conductivity of heat.

Figure 4 is a complete wiring diagram of couples, indicating junctions, selector switch, and potentiometer assembly. Thus, for example, to measure temperature (T_4) it is simply necessary to move selector switch contact bar to A adjust potentiometer until e.m.f. generated by (T_4) is just balanced by standard e.m.f. and record this e.m.f. Referring this reading to the calibration curve, the temperature corresponding to the generated e.m.f. is read off directly.

Temperature Control. As already indicated in previous sections adjustable slide-wire rheostats are used in conjunction with each of the heaters. Two special switch-boards (Figures 1 and 2) not only simplify and facilitate the operation, but make it considerably safer.

The switchboard (above pressure control Figures 1 and 2) has two power lines coming into it (Figure 5). The main line is connected to the safety switch (S_7) which is provided with 30 ampere fuses. The auxiliary line (used to decrease load on main line) comes in through (S_8) (Figure 5). Thus the operator may, by simply changing contact-position of (S_8), draw current for pumps and other auxiliary equipment either from the main line or auxiliary line, the choice depending, of course, on the total load carried by either line at that time.

The main control switchboard (placed to the right of receiver, under manostatic relay (Figures 1 and 2) carries switches (single pole double throw switches are preferred, the double pole double throw type being used simply because they were available at time of construction) by means of which all the heaters, pumps, and other devices are controlled. Furthermore, by proper manipulation, the ammeter may be made to indicate the current flowing through one of the heaters, through all of them, or, if desired, the instrument may be cut out of the line entirely. Figure 5 is the complete wiring diagram, indicating rheostats, switches, and ammeter. When in operation (S_7) is of course closed and (S_8) is thrown in to draw current either from the main line or the auxiliary line.

To draw current through the still heater, the contact bar of (S_1) may be brought to position "a" thereby completing the circuit which includes (R_1) and the still heater, or the switch may be placed in position "b", and (S_2) closed, thereby including the ammeter in circuit. By having all heater switches closed in position "a", they all draw current, but of course the ammeter is not in the circuit. By having them all in position "b" and having switches (S_2), (S_4), and (S_5) closed the total current drawn is indicated by the ammeter.

The pumps are controlled by knob type switches leading to outlets in the side switchboard (above the pressure control, Figures 1 and 2) to which pump cords are plugged in. The pressure control system, receiver system and galvanometer light all draw current from the same outlet as the vacuum pump.

Operation of Still.

1. A charge is introduced into the still through side-neck (A_1), an

adapter and a large funnel being used to prevent splattering. In the case of the crude tar, it may be necessary to warm it up somewhat on a steam bath to make it sufficiently fluid. The still has a capacity of 6000 liters. It has been found experimentally that optimum operation is obtained with a 1150 cc. charge. This leaves sufficient space for the foam to break and removes all possibility of flooding.

2. The receiver system is adjusted. Receivers are arranged about turntable, brass plate is pressed tightly against the bell-jar (by means of screw jack) and fluid beeswax is painted about the joints.

3. Switch (S_{10}) is closed thereby putting the pump and vacuum control system into operation. The relay is adjusted to its required value as described in the section on pressure regulation.

4. Switches (S_7), (S_8), and (S_1) are closed, thereby starting the heater still. Gradually (R_1) is cut out entirely and the full wattage is applied.

5. As soon as the liquid in the still starts boiling (about 20-30 min.) the heating rate is decreased so that the process will continue at an even but not too violent rate.

6. The blower, air heater, and jacket heater are started. The rheostats are adjusted so that the temperature in the air space is a few degrees lower than that expected for the first vapor to appear. (5-8 degrees difference gives best separation.)

7. The water flow is started through reflux control. This of course requires some experience in the handling of the unit.

8. As the distillate starts to come over, rheostats and reflux are further adjusted.

9. After the run is completed all heaters and the blower are cut out.

The vacuum pump, however, is still left on for 10-15 minutes to flush out the condenser.

10. The vacuum pump is stopped and the vacuum broken by admitting air or inert gas, such as carbon dioxide or nitrogen, through stopcock (G_1).

11. The beeswax in the brass-plate is softened by playing a small gas flame gently on the bottom of the plate for a few moments, the screw jack is then lowered, and receiver assembly is lifted out. Receivers containing distillate are removed, new receivers inserted, and the assembly once again is put together.

12. The residue is siphoned out from the still. The scheme used is partially indicated in Figure 1 and 2. A 10 mm. glass tube bent to fit into the bottom of the flask is inserted into the still through (A_1). Pressure tubing connects it to a 3 liter flask equipped with a 2 hole stopper and an inlet and outlet tube (the stopper and tubes, minus the flask, are seen hanging below main switchboard Figures 1 and 2). A sodium hydroxide tower (not seen in figure) and a 4 foot tube 1.5 inches I.D. serving as a calcium chloride tower (seen to left of column) connects the line to the distillation unit and absorbtion system. To operate, stopcock (G) is closed and vacuum pump started. Hot liquid is drawn out into the residue flask. Most of the vapors are absorbed in auxiliary absorbtion towers, and the balance is completely taken care of in the main system previous to reaching the pump.

Occasionally the entire system should be flushed out by refluxing carbon tetrachloride in the column and siphoning out the resulting solution. To remove any accumulated carbon, the system is freed of vapors by cutting out the rheostats in the heaters. Then the still heater is left on until the

temperature rises sufficiently high to burn off carbon. Of course proper precautions must be taken to assure that the system is entirely free of vapor and that the heating and cooling of the still is carried out very slowly and carefully.

V C

LOW CAPACITY UNIT

(For partially refined tar)

Figure 6 illustrates the working assembly of the unit used to "split up" the tar fractions from the large still into smaller interval fractions.

Generally speaking, it is quite similar to the large unit except for size, and a number of modifications and improvements. It also consists of a heater (B), still (A), column (C), reflux control (D), condenser (E), and receiver system (F).

Still and still heater. The still (A) is a 500 cc. round bottom flask provided with a sidenock (A). The same sidenock serves as inlet for feed, means for siphoning out residue and as an opening for introducing a thermometer.

Heating is provided by a 250 watt Cenco heater, (with round bottom into which flask fits). A light layer of asbestos fibre packed between heater coils and still glass forms a cushion on which the still and column rest, and it also of course modifies the heating effect.

Column Assembly. (C) The column proper is 24 inches long and 1 inch I.D. 1 inch from still, it has several small indentations very much the same as larger unit. Its packing consists of 6 inches ceramic Raschig rings 7/16 inches in diameter and 7/16 inches long followed by 12 inches of broken up Raschig ring to form a closer packing. It is interesting to note here that several columns of a smaller diameter were tried and were found entirely impossible to use. For example, with a 0.5 inch I.D. column, it took several hours of violent boiling before any distillate appeared at all. Furthermore,

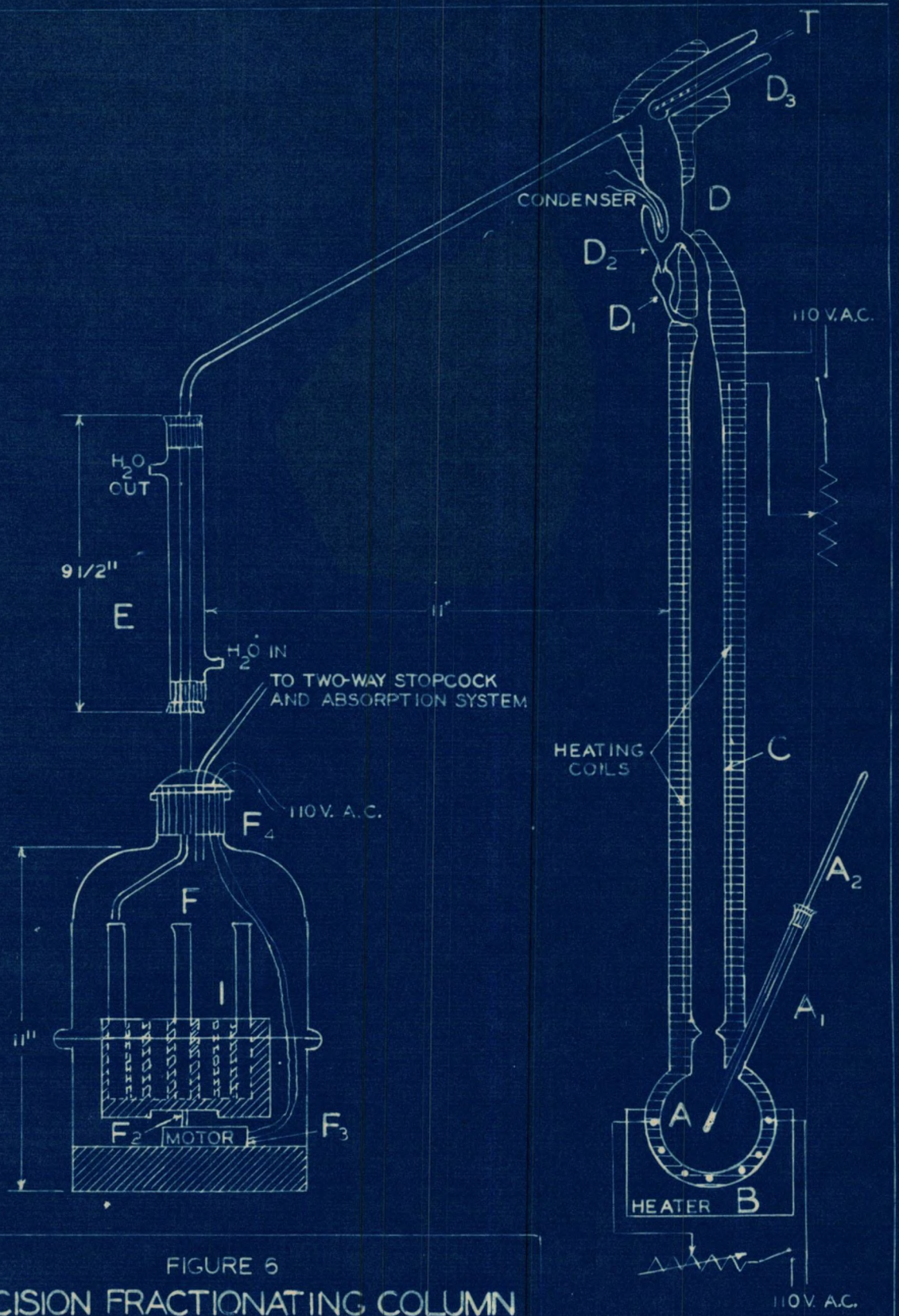


FIGURE 6

PRECISION FRACTIONATING COLUMN FOR LOW TEMPERATURE TARS

LOW CAPACITY UNIT FOR PARTIALLY REFINED TAR OILS

the rate of flow of the vapor, past the couple, was too low, to measure the temperature correctly. Increase of the temperature outside of the column to a point higher than the temperature on the inside invariably resulted in flooding of the system and if left undisturbed, siphoning out of charge from still into condenser system followed. No satisfactory explanation for that effect was found, though it was assumed that it may have been due to surface tension phenomena within column.

The maintenance of proper temperature on the outside of the column also involved some experimentation. An attempt was made to get away entirely from auxiliary heaters by providing the column with a vacuum jacket backed up by 1.5 inches of magnesia insulation. However, that arrangement was found insufficient to prevent loss of heat from the column and was replaced by an auxiliary column heater. (Figure 6). Essentially it consists of 4 No. 24 chromel wire coils connected in series and embedded in 3 inches O.D. 1 inch thick magnesia pipe covering. The pipe covering surrounding the column provides lagging that is supplemented by the heating coils. The latter are connected by means of a switch placed conveniently near the potentiometer assembly and a slide wire rheostat to the 110 A.C. supply.

Reflux Control. The reflux control, (D) embodied in this system is essentially an improved form of the control used with large unit. However, to facilitate the counting of the reflux drops, the condenser terminates in a small funnel (D_2) connected with an inner seal to a bulblet (D_1) which is joined by means of a 3 mm. side tube to column.

In operation all of the vapor condensing within the reflux control, whether it trickles down the condenser wall, or flows down the tube walls, collects in funnel (D_2), passes down into bulblet (D_1) and back to the column

at a point 1.6 inches below its top. To count the reflux it is simply necessary to count drops coming down the funnel tube.

That type of reflux arrangement has two other advantages. The reflux condensate does not come in contact with vapors entering the side condenser and thereby promote additional condensation, and it also helps to cut out mild foaming by providing a comparatively larger space for foam to expand as well as a rapid means for returning it to system without bringing it in contact with fresh vapor.

Condenser. 1/4 inch glass tubing connects the reflux-control to the vertical condenser 9.5 inches long, with an inner tube 1/4 inch I.D. and jacket 1 inch I.D. The vapors sweep past the couple well, down the 1/4 inch tube inclined at 45° to the horizontal and into the condenser placed 11 inches away from the column.

Receiver Assembly. Though the same in principle as the unit already described, it embodies a number of improvements that make for greater ease of operation. Thus, the receiver assembly is housed within a large dessicator (F), 9 inches I.D. and 11 inches high provided with a sufficiently large bottom to accomodate heater motor base and the turntable. In the assembly proper the roller bearing is dispensed with and the turntable is attached directly to a motor shaft, the method of connection being indicated on the diagram. The motor leads come out through one of the holes of the three hole stopper serving to close off top (F_4) of dessicator. Dikhotinsky cement makes the top vacuum tight. (4 feet of wire are bundled up within dessicator, so that bottom could be lowered to the floor, without making it necessary to disconnect the leads).

The two halves of the dessicator are pressed together by a screw jack (the same as in the case of bell jar). Ordinary high vacuum grease is used at the joint thereby dispensing with any necessity of melting wax, or heating glass. Since in normal operation no vapors or liquids are likely to strike the joint, and since the dessicator is at room temperature stopcock grease is quite satisfactory.

Temperature regulation. The still temperature is measured with the thermometer (A_2). The temperature of condensing vapor is noted by means of a copper-constantan Couple (T). The temperature at any point within the column jacket is determined in a somewhat different manner. 1/4 inch holes were drilled through the magnesia covering at regularly spaced intervals throughout height of column. To determine the temperature at any point a thermometer is inserted into the hole nearest to it and the temperature read off. This of course makes it possible to follow the temperature variations throughout the entire height of the system and thereby improve its adjustment.

Temperature adjustment of heater and auxiliary column coils is accomplished by means of rheostats.

Pressure regulation. The same pressure control system is employed as in the larger unit.

Absorbtion train. The same absorbtion train is used as in other units with the exception that the sodium hydroxide tower is by-passed since there is but negligible fuming as is indicated by the absence of irritating odor in gas emanating from pump, as well as to having no effect on wet litmus paper held at the pump outlet tube.

VI

DISTILLATION STUDIES OF TAR

As indicated previously the first series of distillations involved the separation of a working fraction. In order to obtain a better index of the temperature limits that should be selected, and simultaneously to check on the performance of still, several very carefully controlled runs were made, checking on temperature rise, rate of distillation, sensitivity of equipment to changes in rheostat adjustments, reflux variation and other details involved.

In general, it was found that best performance was obtained with a fairly uniform rate of 60-90 drops of distillate per minute and a rather high reflux ratio of 12-16. That reflux ratio had to be gradually decreased as the higher boiling fractions began distilling over. Irrespective of pressure maintained within the system, fixed gases began to form at a still temperature of 290° - 300°C. This rendered any fractions collected at a still temperature higher then 290°C., not representative of the crude.

The results of a 1.5 hour test run are given in Table VI. No attempt is made to graph those results, since only a very exaggerated plot would indicate that the temperature rose in "jumps" and not gradually as in ordinary distillation. This fact can be easily verified by referring to Table VI, and noting that the temperature tended to remain constant for short intervals of time and then rather abruptly rise.

TABLE VI.

Distillation Run of Lehigh Crude Tar

Pressure: 20 mm. Hg. Rate: 60-80 drops per minute. Charge 1000 cc.

Time (min.)	Temperature (°C)	Cumulative volume (cc.)	Volume per minute (cc.)	Cumulative percent of distillate (%)	Time (min.)	Temperature (°C)	Cumulative volume (cc.)	Volume per minute (cc.)	Cumulative percent of distillate (%)
0	94.75	0.0	0.0	0.0	17	119.53	30.75	1.75	3.08
1	100.00	2.5	2.5	0.25	18	120.95	33.00	1.25	3.30
2	101.80	4.45	2.0	0.45	19	122.10	35.0	2.0	3.50
3	102.78	6.0	1.5	0.60	20	123.00	37.0	2.0	3.70
4	103.90	8.0	2.0	0.80	21	123.98	39.2	3.2	3.90
5	105.94	10.0	2.0	1.00	22	124.67	41.5	2.3	4.15
6	106.75	12.0	2.0	1.20	23	126.38	43.5	2.0	4.35
7	106.79	13.0	1.5	1.35	24	127.30	45.50	2.0	4.55
8	106.80	15.0	1.5	1.50	25	127.31	48.25	2.75	4.82
9	107.60	16.5	1.5	1.65	26	127.76	50.0	1.75	5.00
10	108.50	18.0	2.5	1.80	27	128.32	52.25	2.25	5.23
11	109.52	19.75	1.75	1.97	28	129.13	55.0	2.75	5.50
12	110.55	21.50	1.75	2.15	29	129.85	57.0	2.0	5.70
13	111.65	23.0	1.5	2.30	30	130.75	59.5	2.5	5.95
14	112.60	25.0	2.02	2.50	31	131.10	61.25	1.75	6.12
15	114.71	27.0	2.0	2.70	32	131.95	64.25	3.0	6.43
16	116.83	29.0	2.0	2.90	33	132.47	66.75	2.5	6.67

TABLE VI (Continued)

Time (min.)	Temperature (°C)	Cumulative volume (cc.)	Volume per minute (cc.)	Cumulative percent of distillate (%)	Time (min.)	Temperature (°C)	Cumulative volume (cc.)	Volume per minute (cc.)	Cumulative percent of distillate (%)
34	132.95	69.0	2.25	6.90	51	139.01	106.5	2.25	10.65
35	133.55	71.75	2.75	7.18	52	139.55	108.50	2.00	10.85
36	133.85	74.0	2.25	7.40	53	140.20	110.5	2.00	11.05
37	134.12	76.5	2.5	7.65	54	140.35	113.00	2.50	11.30
38	134.38	80.0	3.5	8.00	55	141.06	115.50	2.50	11.55
39	134.58	82.0	2.0	8.20	56	141.58	117.50	2.00	11.75
40	134.69	83.5	1.50	8.35	57	142.11	121.00	3.50	12.10
41	134.84	86.25	2.75	8.62	58	142.55	122.50	1.50	12.25
42	134.84	88.50	2.25	8.85	59	143.25	125.00	2.50	12.50
43	135.25	90.75	2.25	9.08	60	143.68	128.50	3.50	12.85
44	135.72	92.25	1.25	9.22	61	145.91	131.50	3.00	13.15
45	136.40	94.00	1.75	9.40	62	144.46	132.25	0.75	13.22
46	136.56	96.00	2.00	9.60	63	145.08	134.50	2.25	13.45
47	137.30	97.75	1.75	9.77	64	145.20	137.00	2.50	13.70
48	137.71	100.25	2.50	10.03	65	145.40	139.50	2.50	13.95
49	138.10	102.00	1.75	10.20	66	145.74	141.50	2.00	14.15
50	138.50	104.25	2.25	10.42	67	146.78	144.50	3.00	14.45

TABLE VI (Continued)

Time (min.)	Temperature (°C)	Cumulative volume (cc.)	Volume per minute (cc.)	Cumulative percent of distillate (%)	Time (min.)	Temperature (°C)	Cumulative volume (cc.)	Volume per minute (cc.)	Cumulative percent of distillate (%)
68	146.90	147.00	2.50	14.70	80	152.02	176.50	2.75	17.65
69	147.40	149.50	2.50	14.95	81	152.45	179.00	2.50	17.90
70	147.46	152.00	2.50	15.20	82	152.74	181.00	2.00	18.10
71	147.90	154.25	2.25	15.42	83	153.40	183.75	2.75	18.38
72	148.70	156.75	2.50	15.68	84	153.90	186.25	2.50	18.63
73	148.95	159.50	2.75	15.95	85	154.44	188.50	2.25	18.85
74	149.23	161.50	2.00	15.15	86	155.06	191.75	3.25	19.17
75	149.70	164.00	2.50	16.40	87	155.65	194.75	3.00	19.48
76	150.42	166.50	2.50	16.65	88	156.24	196.75	2.00	19.67
77	150.60	169.00	2.50	16.90	89	156.58	198.75	2.00	19.88
78	151.08	171.25	2.25	17.13	90	157.35	200.75	2.00	20.07
79	151.65	173.75	2.50	17.38					

The entire process of reducing the crude to approximately one half degree fractions involved a number of separate steps. First the working fraction was obtained from the crude. It was then fractionated into 10°C intervals. Each of the 10°C fractions was again redistilled in the large unit, cuts being taken every 2.5°C. These fractions, each of which consisted of 50-300cc. of oil were distilled in the small unit into 0.4-0.6 degree intervals. In the following paragraphs each distillation series is summarized separately.

Series A. The crude tar was distilled at a pressure of 20mm. of Hg., only the 125° - 225°C fraction being collected. Using 1000-1500 cc. of crude per charge enough runs were made to collect 7000 cc. of creosote oil.

The working fraction, light brown in appearance, turned dark on standing. It had a sharp unpleasant odor. The specific gravity determined on a fresh sample of distillate was found to be 0.9940 at 20°C. referred to H_2O at 20°C. However although stored in tightly stoppered flasks its specific gravity gradually increased to about 1.0005 at 20°C. It was found that this effect could be accelerated by warming up oil and blowing air through it. Obviously the oxidation of various components of the oil was a major factor in the increase of the specific gravity.

A number of A.S.T.M. distillations were made using samples of the working fraction (creosote oil). The results of two such runs are given in table VII, and Graph A.

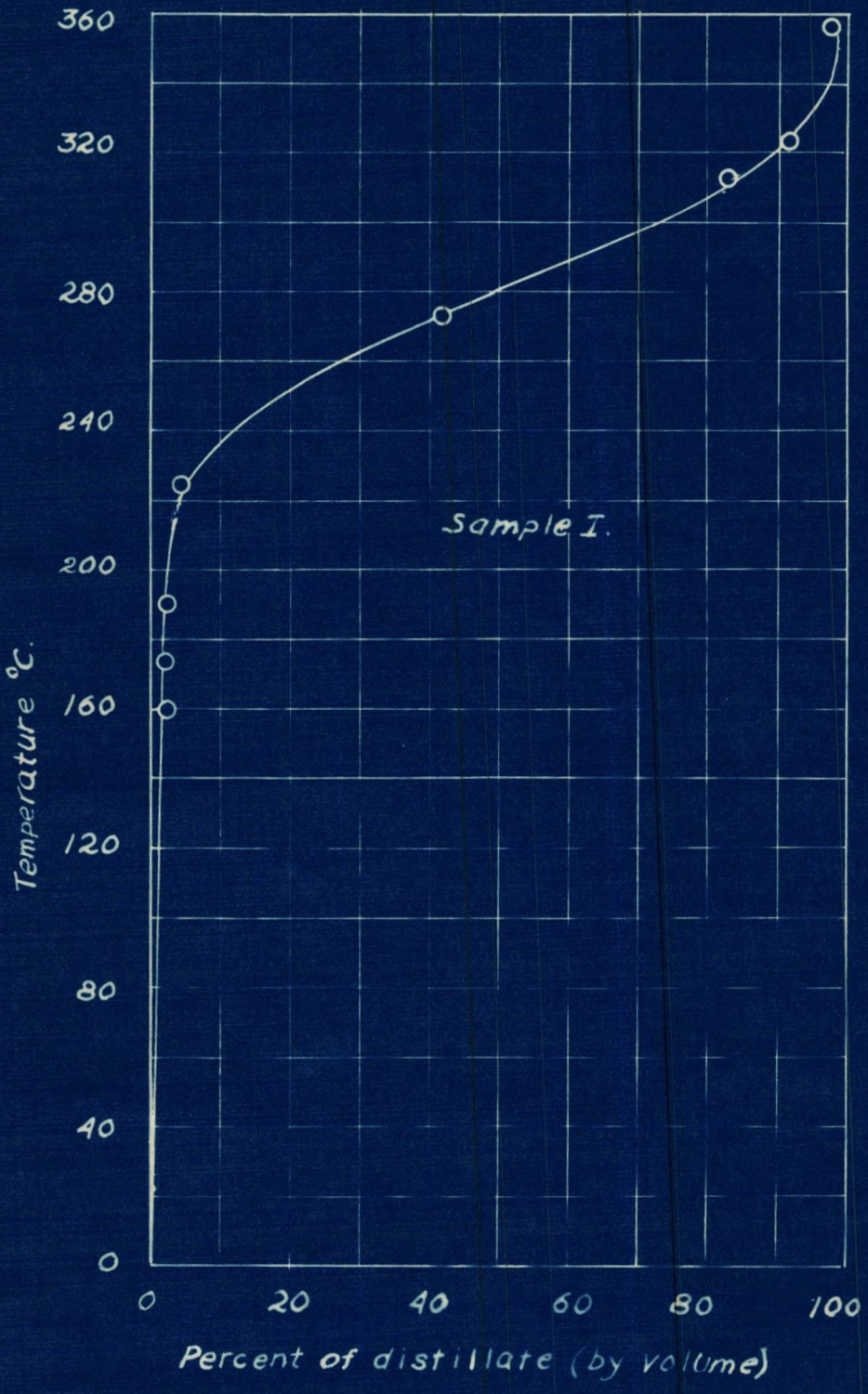
TABLE VII

A.S.T.M. Distillation Results of Working Fraction

(A.S. T.M. Designation D 402 - 36)

Sample Number	I	II
Volume of Sample	100.00cc.	100.00cc.
First Drop Over at	106°C	108.6°C

Temperature Range (degrees centigrade)	Volume (cc.)	Volume percent (%)	Cumulative percent (%)	Volume (cc.)	Volume percent (%)	Cumulative percent (%)
Up to 100° C.	1.6	1.6	1.6	0.6	0.6	0.6
100-175	0.5	0.5	2.0	1.1	1.1	1.6
175-190	0.3	0.3	2.3	0.4	0.4	2.0
190-225	0.7	0.7	3.0	1.1	1.1	3.1
225-275	40.5	40.5	43.5	41.1	41.1	44.2
275-315	40.3	40.3	83.8	40.0	40.0	84.0
315-325	8.2	8.2	92.0	8.5	8.5	92.5
325-360	7.0	7.0	99.0	7.0	7.0	99.5
Residue	0.5	0.5	99.5	0.2	0.2	99.7
Loss	0.5	0.5	100.0	0.3	0.3	100.0



Graph 4. A.S.T.M. distillation curve for working fraction (creosote).

Series B. The creosote oil was fractionated in 1000cc. portions taking cuts every 10°C., and maintaining a pressure 80 mm.Hg. No attempt was made to make any quantitative measurements of the fractions. The first oil coming over was clear and colorless, with successive fractions growing gradually darker, and more opaque to light. On standing for several days all the samples turned dark brown.

Series C. Each of the 10°C cuts was further redistilled in the large unit at 40 mm. Hg. separating these into 2.5 degree intervals. Most of the fractions were colorless and clear, but turned dark and opaque in a few days.

Series D. The 2.5 degree fractions were each put through the small still, and were fractionated into 0.4 - 0.6 degree intervals at a pressure of 10 mm. Hg. In color, the distillate ranged from water clear through light amber and green to light brown.

Testing of Samples

As soon as samples were taken from the receiver turntable, their refractive index was determined at 20°C. using an Abbe refractometer.

Specific gravity determinations were also made. Because of the small size of some of the samples (fraction of cc.) and lack of equipment for microscopic work, it presented somewhat of a problem. However, a number of methods were tried out and one finally adapted that not only was reasonably accurate but also quite rapid and simple. The method is given as follows:

The test tubes containing the samples were lowered into a constant temperature bath, maintained at 20°C. A tall beaker partially filled with water (and clamped on the inside of bath) formed a handy receptacle for the sample tubes. 1 and 2cc. graduated pipettes were then packed into a large

test tube, which also was lowered into the bath, and fastened so that no water could get into the tubes and wet the pipettes.

To determine the specific gravity of any sample, a portion of the oil was carefully pipetted out, without however removing the tube from the bath, and thereby affecting its temperature. Part of the pipette contents was rapidly transferred into a previously tared weighing bottle, care being taken that none of the oil-film adhering to lower end of pipette was rubbed off on wall of bottle. Thus, having the weight of a given volume of oil at a definite temperature, the specific gravity at that temperature could be calculated.

The advantages of this method were several. (1) there was no danger of inaccuracy due to liquid adhering to side of tip. (2) the residual oil after full discharge of pipette could be neglected. (3) because of the small inner diameter of the pipettes used a slight inaccuracy in reading volume did not involve a large error. (4) the method was quite simple and rapid.

The refractive indices and specific gravities are tabulated in Tables VIII and IX.

TABLE VIII

Refractive Indices Of Final Fractions (20°C)

Sample Number	Temperture Range (°C)	Refractive Index I	Index II	Average Ref. Index
1	106.05-106.49	1.5220	1.5220	1.5220
2	106.49-107.08	1.5232	1.5232	1.5232
3	107.08-107.70	1.5236	1.5238	1.5237
4	107.70-108.16	1.5259	1.5257	1.5258
5	108.16-117.40	1.5251	1.5253	1.5252
6	117.40-117.80	1.5242	1.5242	1.5242
7	117.80-118.42	1.5246	1.5247	1.5246
8	118.42-118.85	1.5242	1.5241	1.5241
9	118.85-119.25	1.5240	1.5238	1.5239
10	119.25-119.65	1.5246	1.5247	1.5246
11	119.65-121.55	1.5250	1.5250	1.5250
12	121.55-121.95	1.5257	1.5256	1.5256
13	130.40-130.80	1.5318	1.5318	1.5318
14	130.80-131.20	1.5322	1.5322	1.5322
15	131.20-131.64	1.5322	1.5322	1.5322
16	131.65-132.03	1.5327	1.5327	1.5327
17	132.03-132.41	1.5332	1.5331	1.5331
18	132.41-133.36	1.5335	1.5335	1.5335
19	133.36-133.88	1.5317	1.5317	1.5317
20	133.88-134.60	1.5325	1.5325	1.5325
21	134.60-134.98	1.5321	1.5320	1.5320

TABLE VIII

(Continued)

Refractive Indices of Final Fractions (30°C)

Sample Number	Temperture Range (°C)	Refractive Index I	Index II	Average Ref. Index
22	134.98-135.35	1.5324	1.5324	1.5324
23	135.35-135.90	1.5335	1.5335	1.5335
24	135.90-136.30	1.5387	1.5387	1.5387
25	136.30-136.71	1.5342	1.5342	1.5342
26	136.71-137.12	1.5411	1.5411	1.5411
27	137.12-137.65	1.5411	1.5411	1.5411
28	139.99-140.40	1.5338	1.5338	1.5338
29	140.40-140.82	1.5347	1.5347	1.5347
30	140.82-141.21	1.5409	1.5409	1.5409
31	141.21-142.68	1.5354	1.5354	1.5354
32	142.68-143.62	1.5368	1.5367	1.5368
33	145.01-145.40	1.5365	1.5365	1.5365
34	145.40-145.79	1.5372	1.5373	1.5372
35	145.79-146.40	1.5379	1.5380	1.5380
36	146.40-146.81	1.5374	1.5374	1.5374
37	147.20-147.60	1.5378	1.5378	1.5378
38	147.60-148.03	1.5380	1.5380	1.5380
39	148.03-148.41	1.5390	1.5389	1.5389
40	148.41-148.84	1.5385	1.5385	1.5385
41	148.84-149.22	1.5441	1.5439	1.5440
42	149.22-149.60	1.5442	1.5441	1.5441

TABLE VIII (Continued)

Refractive Indices of Final Fractions (20°C)

43	149.60-150.02	1.5447	1.5448	1.5447
44	150.02-150.41	1.5451	1.5452	1.5451
45	150.41-150.81	1.5448	1.5449	1.5448
46	152.02-152.55	1.5464	1.5465	1.5464
47	152.55-152.95	1.5467	1.5468	1.5467
48	152.95-153.35	1.5475	1.5475	1.5475
49	153.35-153.81	1.5473	1.5474	1.5473
50	153.81-154.18	1.5497	1.5497	1.5496
51	154.19-154.64	1.5489	1.5488	1.5488
52	154.64-154.98	1.5459	1.5459	1.5459
53	154.98-155.36	1.5462	1.5463	1.5462
54	155.36-155.75	1.5471	1.5472	1.5471
55	155.75-156.35	1.5467	1.5469	1.5468
56	156.35-156.92	1.5468	1.5468	1.5468
57	156.92-157.51	1.5466	1.5467	1.5466
58	157.51-157.91	1.5432	1.5432	1.5432
59	157.91-158.31	1.5454	1.5454	1.5454
60	158.31-158.70	1.5464	1.5464	1.5464
61	158.70-159.30	1.5470	1.5468	1.5467
62	159.30-159.80	1.5473	1.5473	1.5473
63	159.80-160.46	1.5473	1.5472	1.5472
64	160.46-161.05	1.5498	1.5498	1.5498
65	161.05-161.65	1.5498	1.5498	1.5498
66	161.65-162.24	1.5494	1.5495	1.5494
67	162.24-162.61	1.5496	1.5496	1.5496

TABLE VIII (Continued)

Refractive Indices of Final Fractions (20°C)

68	163.61-163.21	1.5497	1.5496	1.5497
69	163.21-163.60	1.5547	1.5547	1.5547
70	163.60-164.01	1.5540	1.5539	1.5539
71	164.01-164.60	1.5546	1.5546	1.5546
72	164.60-165.20	1.5500	1.5500	1.5500
73	165.80-166.37	1.5651	1.5651	1.5651
74	166.37-167.81	1.5651	1.5651	1.5651
75	167.81-168.31	1.5494	1.5494	1.5494
76	168.31-168.70	1.5480	1.5480	1.5480
77	168.70-169.28	1.5472	1.5472	1.5472
78	169.28-169.65	1.5477	1.5477	1.5477
79	169.65-170.06	1.5489	1.5487	1.5488
80	170.06-170.65	1.5486	1.5486	1.5486
81	171.62-172.76	1.5489	1.5489	1.5489
82	172.21-172.76	1.5495	1.5495	1.5495
83	172.76-173.40	1.5512	1.5512	1.5512
84	173.40-174.52	1.5516	1.5516	1.5516
85	174.52-174.91	1.5519	1.5519	1.5519
86	174.91-175.40	1.5524	1.5524	1.5524
87	175.40-175.89	1.5525	1.5525	1.5525
88	175.89-176.40	1.5520	1.5520	1.5520
89	176.40-176.85	1.5505	1.5505	1.5505
90	176.85-178.10	1.5475	1.5475	1.5475
91	178.10-178.60	1.5480	1.5480	1.5480

TABLE VIII (Continued)

Refractive Indices of Final Fractions (20°C)

92	178.60-179.09	1.5500	1.5500	1.5500
93	179.09-179.59	1.5502	1.5501	1.5502
94	179.59-180.05	1.5479	1.5479	1.5479
95	180.05-180.52	1.5483	1.5482	1.5482
96	180.52-181.00	1.5491	1.5490	1.5490
97	181.00-181.46	1.5490	1.5491	1.5490
98	181.46-181.95	1.5494	1.5494	1.5494
99	181.95-182.45	1.5494	1.5495	1.5494
100	182.45-183.01	1.5594	1.5595	1.5594
101	183.01-183.56	1.5500	1.5499	1.5499
102	183.56-183.95	1.5502	1.5501	1.5501
103	183.95-184.35	1.5421	1.5420	1.5490
104	184.35-184.71	1.5502	1.5503	1.5502
105	184.71-185.20	1.5534	1.5533	1.5533
106	185.20-185.67	1.5535	1.5534	1.5534
107	185.67-186.05	1.5515	1.5515	1.5515
108	186.05-186.60	1.5491	1.5490	1.5490
109	186.60-187.21	1.5467	1.5467	1.5467
110	187.21-187.51	1.5488	1.5487	1.5487
111	187.95-188.45	1.5567	1.5568	1.5567
112	188.45-188.91	1.5573	1.5572	1.5572
113	188.91-189.40	1.5576	1.5576	1.5576
114	189.40-189.87	1.5579	1.5579	1.5579
115	189.87-190.35	1.5580	1.5581	1.5580

TABLE VIII (Continued)

Refractive Indices of Final Fractions (20°C)

116	190.35-190.62	1.5582	1.5582	1.5582
117	190.62-191.30	1.5586	1.5586	1.5586
118	191.30-191.78	1.5586	1.5585	1.5585
119	191.78-192.25	1.5587	1.5587	1.5587
120	192.25-192.75	1.5587	1.5586	1.5586
121	192.75-193.20	1.5589	1.5590	1.5589
122	193.20-193.71	1.5586	1.5586	1.5586
123	193.71-194.18	1.5594	1.5593	1.5593

TABLE IX

Specific Gravities of Final Fractions

(at 20°C referred to H_2O at 20°C)

Sample Number	Temperature Range (°C)	Vial & Sample (gm.)	Vial (gm.)	Sample (gm.)	Volume of Sample (cc.)	Specific Gravity of Oil (gm./cc.)
1	106.06-106.49					
2	106.49-107.08					
3	107.08-107.70					
4	107.70-108.16		METHOD USED FOUND			
5	108.16-117.40		NOT RELIABLE. NOT			
6	117.40-117.80		ENOUGH OIL WAS LEFT			
7	117.80-118.42		FOR SECOND ANALYSIS			
8	118.42-118.85		BY MEANS OF METHOD			
9	118.85-119.25		FINALLY ADAPTED.			
10	119.25-119.65		THE SAME REASONS AS			
11	119.65-121.55		INDICATED ABOVE AP-			
12	121.55-121.95		PLY TO THE OTHER			
13	130.40-130.80		BLANKS IN THE TABLE.			
14	130.80-131.20					
15	131.20-131.65					
16	131.65-132.03	28.6526	28.3642	0.2884	0.3	0.96295
17	132.03-132.41					
18	132.41-133.36					
19	133.36-133.88					
20	133.88-134.60					

TABLE IX (Continued)

Sample Number	Temperature Range (°C)	Vial & Sample (gm.)	Vial (gm.)	Sample (gm.)	Volume of Sample (cc.)	Specific Gravity of Oil (cc.)
21	134.60-134.98					
22	134.98-135.35	28.3642	28.0651	0.2991	0.3	0.9990
23	135.35-135.90					
24	135.90-136.30					
25	136.30-136.71					
26	136.71-137.12					
27	137.12-137.65					
28	139.99-140.40	11.4892	11.1966	0.2926	0.3	0.9769
29	140.40-140.82					
30	140.82-141.21					
31	141.21-142.66					
32	142.66-143.62					
33	145.01-145.40					
34	145.40-145.79					
35	145.79-146.40	28.8851	28.9897	0.8954	0.4	0.99025
36	146.40-146.81					
37	147.20-147.60					
38	147.60-148.03	9.3741	9.0766	0.2975	0.3	0.9933
39	148.03-148.41					
40	148.41-148.84					
41	148.84-149.22	28.9496	27.9196	1.0300	1.0	1.020

TABLE IX (Continued)

Sample Number	Temperature Range (°C)	Vial & Sample (gm.)	Vial (gm.)	Sample (gm.)	Volume of Sample (cc.)	Specific Gravity of Oil
42	149.22-149.60	9.0760	8.5691	0.5169	0.5	1.0357
43	149.60-150.02	28.7075	28.2089	0.4986	0.5	0.9990
44	150.02-150.41	12.1932	11.6549	0.5383	0.5	1.0784
45	150.41-150.81	10.2256	9.1999	1.0257	1.0	1.0273
46	152.02-152.55	28.1254	27.9235	0.2019	0.2	1.0115
47	152.55-152.95	27.6528	2714552	0.9072	0.9	0.9990
48	152.95-153.35	29.0129	28.1057	0.9072	0.9	1.0098
49	153.35-153.81	26.9712	27.9787	0.9926	1.0	0.9943
50	153.81-154.19	12.7675	11.8685	0.9080	1.0	0.9066
51	154.19-154.64	27.3676	27.601	0.3075	0.3	1.0268
52	154.64-154.98	28.2406	27.9413	0.2995	0.3	1.0000
53	154.98-155.36	11.1966	10.7285	0.3681	0.4	0.9219
54	155.36-155.75	11.3321	11.1372	0.1949	0.2	0.9764
55	155.75-156.35	11.1915	10.4631	0.7284	0.7	1.0425
56	156.85-156.92	29.1406	28.0401	1.1005	1.0	1.0119
57	156.92-157.51	11.4170	10.3840	1.0330	1.0	1.0160
58	157.51-157.91	12.2507	11.1105	1.1402	1.0	1.1420
59	157.91-158.31	28.1399	27.6466	0.4953	0.5	0.9928
60	158.31-158.70	11.9771	11.4170	0.5601	0.6	0.9374
61	158.70-159.30	11.0100	10.5555	0.4545	0.5	0.9318
62	159.30-159.80	28.7973	28.4800	0.3175	0.3	1.0352
63	159.80-160.46	10.9355	10.6355	0.3020	0.3	1.0084

TABLE IX (Continued)

Sample Number	Temperature Range (°C)	Vial & Sample (gm.)	Vial (gm.)	Sample (gm.)	Volume of Sample (cc.)	Specific Gravity of Oil (gm.)
64	160.46-161.06	28.[illegible]87	27.9380	0.5547	0.5	1.1116
65	161.06-161.65	161				
66	161.65-162.24					
67	162.24-162.81					
68	162.81-163.21					
69	163.21-163.60					
70	163.60-164.01					
71	164.01-164.60	29.1462	28.9496	0.1966	0.2	0.9819
72	164.60-165.20					
73	165.80-166.37					
74	166.37-167.81	27.7902	27.5015	0.2887	0.3	0.9639
75	167.81-168.31					
76	168.31-168.70					
77	168.70-169.28					
78	169.28-169.65					
79	169.65-170.06					
80	170.00-170.65					
81	171.62-172.21					
82	172.21-172.76					
83	172.76-173.40	28.5421	28.0217	0.5204	0.5	1.0425
84	173.40-174.52	10.7898	10.5901	0.1995	0.2	0.9969
85	174.52-174.91	11.0926	10.5596	0.5330	0.5	1.066

TABLE IX (Continued)

Sample Number	Temperature Range (°C)	Vial & Sample (gm.)	Vial (gm.)	Sample (gm.)	Volume of Sample (cc.)	Specific Gravity of Oil (cc.)
86	174.91-175.40	10.0772	9.7785	0.2987	0.3	0.9995
87	175.40-175.89	8.5353	8.3400	0.1953	0.2	1.0071
88	175.89-176.40	28.4430	27.6812	0.7038	0.7	1.0020
89	176.40-176.85	28.4208	28.0207	0.4001	0.4	1.1605
90	176.85-178.10	28.8559	28.0449	0.8110	0.7	0.9631
91	178.10-178.60	28.3969	27.9162	0.4807	0.5	1.0649
92	178.60-179.09	28.3152	28.2089	0.1063	0.1	1.0603
93	179.09-179.59	28.3837	28.0662	0.3175	0.3	1.1548
94	179.59-180.05	28.0359	27.5195	0.5664	0.5	1.0925
95	180.05-180.52	9.7675	9.2242	0.5431	0.5	0.9967
96	180.52-181.00	10.9064	10.6077	0.2987	0.3	1.0035
97	181.00-181.46	9.863	9.4616	0.4007	0.4	1.0195
98	181.46-181.95	29.4090	29.2055	0.2035	0.2	0.8305
99	181.95-182.45	8.7520	8.5611	0.1909	0.2	0.9694
100	182.45-183.01	28.9065	28.0336	0.8729	0.9	1.0195
101	183.01-183.56	28.9312	27.9234	1.0078	1.0	1.0486
102	183.56-183.95	12.6135	10.5205	2.0930	2.0	0.9857
103	183.95-184.35	9.5601	9.4617	0.0984	0.1	0.8954
104	184.35-184.71	30.0929	29.1991	0.8938	1.0	1.0051
105	184.71-185.20	11.4966	10.4930	1.0035	1.0	1.0053
106	185.20-185.67	10.7697	10.5696	0.2001	0.2	1.0025

TABLE IX (Continued)

Sample Number	Temperature Range (°C)	Vial & Sample (gm.)	Vial (gm.)	Sample (gm.)	Volume of Sample (cc.)	Specific Gravity of Oil (cc.)
107	185.67-186.05	28.6583	28.4430	0.2153	0.2	1.0784
108	186.05-186.60	28.3303	28.0208	0.3095	0.3	1.0317
109	186.60-187.21	29.6564	28.6575	0.9991	1.0	1.0008
110	187.21-187.57	27.9913	27.7880	0.2033	0.2	1.0135
111	187.95-188.45	11.7140	10.8109	0.9031	1.0	0.9047
112	188.45-188.91	11.7507	11.6140	0.1367	0.1	1.3695
113	188.91-189.40	28.7677	27.7126	1.0551	1.0	1.0559
114	189.40-189.87	9.4382	9.2238	0.2144	0.2	1.0741
115	189.87-190.35	11.4867	10.6372	0.8495	0.8	1.0627
116	190.35-190.82	28.4148	28.0993	0.3155	0.3	1.0525
117	190.82-191.30	28.8028	28.3152	0.4876	0.5	0.9771
118	191.30-191.78	11.8625	10.8591	1.0034	1.0	1.0053
119	191.78-192.25	29.0881	28.0850	1.0031	1.0	1.0048
120	192.25-192.75	10.4631	9.4610	1.0021	1.0	1.0037
121	192.75-193.20	11.0878	10.5580	0.5298	0.5	1.0533
122	193.20-193.71	28.0233	27.9230	0.1003	0.1	1.0050
123	193.71-194.18	11.0756	10.7896	0.2860	0.3	0.9549

Even a casual analysis of the series of refractive indices and the specific gravities, indicates the difficulty of identifying fractions without additional information. The densities and refractivities of the various compounds are too close together to be used as an index for the segregation of the fractions. Additional difficulty was encountered due to the fact that in none of the available tables listing physical constants of organic substances, was there any common reference temperature at which the constants were reported.

Generally speaking the following additional information was thought necessary to identify the fractions: (1) molecular weights (conveniently obtained by the lowering in freezing pt. method, using a suitable solvent) (2) boiling points (3) freezing points. (4) where possible, crystallization of the oil and a study of the crystals. As final proof of the identity of certain compounds "mixed boiling points and melting points" could be employed. A preliminary determination as to whether a given oil is an aldehyde, ketone, paraffin, etc. or whether it is saturated or unsaturated would naturally simplify search through the tables of physical constants.

Lack of facilities and equipment as well as lack of time prevented the carrying through of the work outlined in the previous paragraph.

VII

GENERAL SUMMARY

The problem on hand involved, primarily, the development of high precision fractional distillation equipment for low temperature tar, obtained as a by-product in the carbonization of North Dakota lignite. The second phase of the research dealt with actual distillations of the cruse in an attempt to separate out individual compounds to be identified by certain of their characteristic physical constants.

By far the greater portion of the total time devoted to the research was spent in developing a compact, efficient, semi-automatic laboratory low temperature tar distillation unit.

The value of such an analytical still depends mainly on its degree of separation and simplicity of operation. However, the two above mentioned requirements depend on a number of other factors, each of which tends to add or detract from the value of unit. To mention only a few of the more important ones, accuracy of temperature measurement and regulation, pressure control, reflux ratio adjustment, rate of distillation, type of packing used, thermal conditions outside of column, lagging, etc., all have an important bearing on the behavior of the still. With a greasy, rather unstable mixture such as lignite tar the problem is even more difficult, for precautions must be taken that no decomposition takes place, that vapors do not strike any material they are likely to interact with, that absolutely no air be allowed to come in contact with condensing vapors, etc.,

Two units were developed, one with a maximum still capacity of 6000cc.

for handling the crude, and the other with maximum capacity of 500cc. to be used for the closer fractionation of samples from the large still. Both units were constructed entirely of pyrex glass, and were found quite satisfactory from the standpoint of accuracy as well as mechanical performance.

Using thermocouples with a sensitive galvanometer the temperatures could easily be estimated to 0.02°C. The pressure was maintained for hours within a fraction of a millimeter, without any attention from the operator. By means of rheostats, the temperature and hence rate of distillation could be varied within a reasonable range, best results being obtained with a temperature difference of 5-6 degrees between temperature of vapor and that outside of column.

The optimum distillation rate was found to be between 60-80 drops of distillate per minute. Slower rates affected the accuracy of the thermocouple readings while faster rates made it difficult to follow temperature variations and affected the sharpness of separation.

The reflux regulators developed were very satisfactory from the standpoint of efficiency, ease of adjustment, and observation. Best results were obtained using a reflux ration of 12-15.

The receiver system in its final form is suitable for materials such as lignite tar, though it cannot be used where extremely volatile liquids are involved, for large empty space above the receiver tubes promotes flash vaporization.

To identify the final samples (from the small still) their refractive indices and specific gravities were determined.

However they were too close together to be of great value. Lack of time and facilities prevented further work on the samples, which therefore remained unidentified.

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